SEARCH REQUEST FORM

Scientific and Technical Information Center

. =	N . 4 10 C .	Eveniner#.	62294	Date: 9/4/	04
Requester's Full Name:Phot				674737	
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If more than one search is su	ıbmitted, please priori ********	tize searcnes !! *******	n order of ne	:ea. *********	*****
Please provide a detailed statement of Include the elected species or structur utility of the invention. Define any te known. Please attach a copy of the co	f the search topic, and descril res, keywords, synonyms, act rms that may have a special	be as specifically as ronyms, and registry meaning. Give exa	s possible the sub y numbers, and o emples or relevan	oject matter to be sombine with the	searched. concept or rs, etc, if
Title of Invention: LITHI	in ION SECONDAM	y CEU		Tech. Info. Cntr	
Inventor≰ (please provide full name	s): HYO AZUMA	}	SISI	P 7	
inventory (picuse provide rain insert			V.		
Earliest Priority Filing Date:	SGAT, 30 2002		Pat	. & T.M. Office	
For Sequence Searches Only Please a appropriate serial number.		on (parent, child, divi	sional, or issued p	patent numbers) alo	ong with the
A lit	chium ion secondar	ry cell comp	rising a p	ositive	ı
electrode, a n	egative electrode	and a non-a	queous el	ectrolytic	
solution where	ein said negative	electrode c	omprises a	negative	
	ive material conta				
having a spaci	ng d ₀₀₂ of 0.3360	nm or less w	here the s	spacing door	
is a plane dist	ance of (002) plane	es measured b	y a X-ray d	iffraction	
method, a crys	tal size Lc in the	e c-axis dire	ection of a	t least 70	
	ue of from 0.01 t				
of I ₁₃₅₀ to I ₁₅₈₀	in which I ₁₃₅₀ and	I ₁₅₈₀ are Rama	n intensit	ies around	
	1580 cm ⁻¹ in a Rama				
a carbonaceous	s material with an	argon laser	having a	wavelength	
	nd wherein said no				
contains 0.5	to 5% by weight o	f vinylene c	arbonate o	or its	
derivative		_			
AUO: negati	ve electrode comp	rises a mixtu	re of a cel	lulose o	IN A CHEMBERT
ether compound and	l a butadiene copo	olymer rubbe	r as a bin	der.)	*****
STAFF USE ONLY	Type of Search	Ver	idors and cost v	vhere applicable	
Searcher: HARRISON	NA Sequence (#)	STN			
Searcher Phone #: 22511	AA Sequence (#)				
Searcher Location: Jef 4B6	Structure (#)				
Date Searcher Picked Up: 9 - 16	Bibliographic L	Dr.Link			
Date Completed: 9-17-0	Litigation	Lexis/Nexis			
Searcher Prep & Review Time:	Fulltext	Sequence Syste	20		
Clerical Prep Time:	Patent Family	WWW/Internet	,		
Online Time:	Other	Other (specify)	<u> </u>		

PTO-1590 (8-01)



STIC Search Report

STIC Database Tracking Number: 131766

TO: John Maples

Location: REM-6C89 September 17 2004

AU 1745

Case Serial No.: 10/671,737

From: Jeff Harrison

Location: STIC-EIC2800

JEF-4B68

Phone: 22511

Email: harrison, jeff

Search Notes

Examiner Maples,

Re: Graphite in negative electrode in Li secondary cell.

Attached are edited results from patent and nonpatent literature.

I've included some chunks from reference books about graphite.

If you'd like additional searching or explanation, let me know.

Respectfully, Jeff

Jeff Harrison Team Leader, STIC-EIC2800 JEF-4B68, 571-272-2511



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	\bullet	71	
		= 1	
	• 1	V A	•

Questions about the scope or the results of the search? Contact the EIC searcher or contact:

Jeff Harrison, EIC 2800 Team Leader 571-272-2511, JEF 4B68

Voluntary Results Feedback Form
> I am an examiner in Workgroup: Example: 2810
 ➤ Relevant prior art found, search results used as follows: 102 rejection 103 rejection Cited as being of interest. Helped examiner better understand the invention. Helped examiner better understand the state of the art in their technology.
Types of relevant prior art found: Foreign Patent(s) Non-Patent Literature (journal articles, conference proceedings, new product announcements etc.)
 ➢ Relevant prior art not found: ☐ Results verified the lack of relevant prior art (helped determine patentability).
Results were not useful in determining patentability or understanding the invention. Comments:

Drop off or send completed forms to STIC/EIC2800, CP4-9C18



```
FILE 'HCAPLUS' ENTERED
                       L47 OR L52 OR L58 OR L63 OR L61 OR (L64 OR L65 OR L66 OR L67 OR L68 OR L69 OR
            47 S
L77
L70 OR L71) OR (L73 OR L74 OR L75 OR L76)
                       ?CRYST?(6A) PYROL######## (3A) (GRAPHIT###### OR CARBONAC####### OR "C" OR CARBON)
L78
           741 S
                       PYROL####### (6A) (GRAPHIT##### OR CARBONAC####### OR "C" OR CARBON) (6A) ?CRYST?
L79
            837
                      (L40 OR L41 OR L42 OR L43 OR L44 OR L45 OR L46 OR L47 OR L48 OR L49 OR L50 OR
            597 S
L80
L51 OR L52) OR (L56 OR L57 OR L58 OR L59 OR L60 OR L61 OR L62 OR L63 OR L64 OR L65 OR L66 OR L67 OR
L68 OR L69 OR L70 OR L71 OR L72 OR L73 OR L74 OR L75 OR L76 OR L77)
             0
                       L79 AND L80
                       (PYROL########## OR GRAPHIT##### OR CARBONAC####### OR "C" OR
             35
                S
CARBON) (3A) ?CRYST? AND L80
                       L82 NOT L77
             7 S
L83
                       (L10 OR L11 OR L12 OR L13 OR L14 OR L15 OR L16 OR L17 OR L18 OR L19 OR L20 OR
            119
L84
                  S
                       L21 OR L22 OR L23 OR L24) AND (CRYST######### OR MONOCRYST#########)
                       (4A) (700 OR 750 OR 800 OR 850 OR 900 OR 950 OR 1000 OR MM OR NM OR 70 OR 75 OR
                             80 OR 85 OR 90 OR 95 OR 100 OR 71 OR 69 OR 72 OR 73 OR 74)
L85
            109
                       L84 NOT (L82 OR L77)
                S
                       (L1 OR L2 OR (L32 OR VINYLENE CARBONATE OR ?DIOXOL?)) AND L85
L86
                                            28 TERMS
                SEL PLU=ON L8 1- RN :
L87
     FILE 'REGISTRY' ENTERED
             28
                S
                       1.87
L88
              8
                  S
                       L88 AND LI/ELS, MAC
L89
     FILE 'HCAPLUS' ENTERED
             18 S
                       L89 AND L85
1.90
                       L85 AND (1350 OR 1580 OR I1350 OR I1580)
                 S
L91
                S L85 AND (AR OR ARGON OR 514 OR 5145 OR ARGON/CN)
     FILE 'REGISTRY' ENTERED
              1 S
                      ARGON/CN
1.92
     FILE 'HCAPLUS' ENTERED
          90402 S
L93
                       L85 AND (AR OR ARGON OR 514 OR 5145 OR L93)
             5
                  S
L94
                       L86 OR (L90 OR L91) OR L94
L95
             30
                  S
                       HIGH###(2W)(CRYST######### OR ORDER########)(2W)(GRAPHIT###### OR "C" OR
L96
            612
                  S
CARBON OR CARBONAC?)
                       (GRAPHIT###### OR "C" OR CARBON OR CARBONAC?) (3W) HIGH### (2W) (CRYST######### OR
            450
                  S
L97
ORDER########)
                       HIGH###(3W)(GRAPHIT###### OR "C" OR CARBON OR CARBONAC?)(3W)(CRYST######## OR
ORDER########)
                       L85 NOT L95
L99
             79
                 S
                       (L96 OR L97 OR L98) AND L99
                S
L100
             3
                       GRAPHIT####### (3A) PARTIC##########
L101
           6348
                 S
L102
             76
                 S
                       L99 NOT L100
                       L101 AND L102
L103
              3
                 S
                       L102 NOT L103
             73
                 S
L104
             24
                 S
                       L104 AND (002 OR D002)
L105
                       L105 AND (HIGH#### OR SIXE### OR LARG###### OR GREATER)
L106
             9
                 S
                       (L105 AND (HIGH#### OR SIZE### OR LARG###### OR GREATER)) NOT L106
             12
L107
                       L77 OR L83 OR L95 OR L100 OR L103 OR L106 OR L107
                S
L108
            111
                SEL PLU=ON L108 1- PRN :
                                              145 TERMS
L109
     FILE 'WPIX, JAPIO, EUROPATFULL, PCTFULL' ENTERED
            229
                 S
                       L109
L110
                       L110 AND (1350 OR 1580 OR I1350 OR I1580)
L111
             23
                  S
                       L110 AND (002 OR D002)
L112
             94
                       L110 AND (CRYST########## OR MONOCRYST? OR POWDER### OR PARTICULAT##### OR
              9
                  S
L113
                       PARTICLE) (7A) (7O OR 75 OR 80 OR 85 OR 90 OR 95 OR 100 OR 71 OR 69 OR 72 OR 73
                       OR 74) (W) (NM OR NANOM#######)
                       L110 AND (CRYST########## OR MONOCRYST? OR POWDER### OR PARTICULAT##### OR
            123
1.114
                       PARTICLE) (5A) (SIZE## OR SIZING## OR DIMENSION#### OR VOLUME## OR HEIGHT## OR
                       HIGH#### OR LARGE##### OR ENLARG#### OR LONG#### OR LENGTH####)
                       L111 AND L112
L115
             14
                  S
             9
                       L114 AND L115
                  S
L116
                       L113 AND ((L111 OR L112) OR L114)
              8
                  S
L117
             13
                S
                       (L116 OR L117)
L118
```

```
FILE 'REGISTRY' ENTERED
L32
        123437 S
                    16.326.1/RID OR 16.326.4/RID
                s
                      L32 AND 1 3
L33
         100235
         41023 S
                     L32 AND DIMETHYL
L34
     FILE 'HCAPLUS' ENTERED
                      (L12 OR L13 OR L21 OR L24) AND (L25 OR L26 OR L27 OR L28 OR L29)
           320
                S
L35
                      (L12 OR L13 OR L21 OR L24) AND (RAMAN### OR DIFFRACT#### OR X RAY OR 1350 OR
           2372
L36
1580 OR R VALUE OR RATIO OR D002 OR 002 OR PLANES OR 336 OR 335 OR 3350 OR 3360)
            48 S (L12 OR L13 OR L21 OR L24) AND (514(W)5 OR (AR OR ARGON)(2A)(LASING OR LASE##
OR LIGHT OR BEAM))
                      (L14 OR L15 OR L16 OR L17 OR L18 OR L19) OR L23 OR (L35 OR L36 OR L37)
          3784 S
L38
                      L38 AND L31
L39
           2284 S
                S
                      (L32 OR VINYLENE CARBONATE OR ?DIOXOL?) AND L39
L40
            559
                       (L25 OR L26 OR L27 OR L28 OR L29) AND L40
L41
            37
                 S
                       (NONAQUEOUS OR NON AQ OR NON(W)(AQ OR AQUEOUS) OR ORGANIC## OR SOLUTION OR
                s
            356
L42
LIQUID OR FLUID OR SOLVENT) (3A) ELECTROLYT########### AND L40
                      ACTIVE AND L40
            144 S
L43
                      L4(L)(LARGE### OR HIGH#### OR WELL OR QUALITY OR ORDER#### OR STRUCTUR### OR
                S
L44
            36
MORPHOL##### OR SIZE## OR DIMENSION#### OR LONG#### OR LENGTH####) AND L40
            63 S GRAPHIT###(3A)(LARGE### OR HIGH#### OR WELL OR QUALITY OR ORDER#### OR
L45
STRUCTUR### OR MORPHOL##### OR SIZE## OR DIMENSION#### OR LONG#### OR LENGTH####) AND L40
                      (CRYST######### OR MONOCRYST#######) (4A) CARBONAC#####(3A) (LARGE### OR HIGH####
             0 S
L46
OR WELL OR QUALITY OR ORDER#### OR STRUCTUR### OR MORPHOL##### OR SIZE## OR DIMENSION#### OR LONG####
OR LENGTH####) AND L40
                       (CRYST######## OR MONOCRYST#######) (4A) CARBON(3A) (LARGE### OR HIGH#### OR
             5 S
WELL OR QUALITY OR ORDER#### OR STRUCTUR### OR MORPHOL##### OR SIZE## OR DIMENSION#### OR LONG#### OR
LENGTH####) AND L40
                      L41 AND (L42 OR L43 OR L44 OR L45 OR L46 OR L47)
            30 S
1.48
                      L42 AND (L43 OR L44 OR L45 OR L46 OR L47)
            129 S
L49
            16 S
19 S
2 S
                      L43 AND (L44 OR L45 OR L46 OR L47)
L50
                      L44 AND (L45 OR L46 OR L47)
L51
                      L45 AND (L46 OR L47)
T.52
     FILE 'REGISTRY' ENTERED
           3621 S
                      CELLULOS#### AND ETHER
L53
                      BUTADIENE AND (RUBBER OR ELASTOMER)
           212
                S
T.54
                      BUTADIENE AND (COPOLYMER OR ("POLYMER WITH" OR 2-3/NC))
L55
          14143 S
     FILE 'HCAPLUS' ENTERED
                      L40 AND (L53 OR ?CELLULOS? (2A) ETHER)
             11 S
L56
                      L40 AND ((L54 OR L55) OR ?BUTADIEN?(3A)(COPOLYMER######## OR CO
L57
             15
                 S
POLYMER######## OR RUBBER OR ELASTOMER#####))
                S
                      L56 AND L57
             6
L58
                      L37 OR L41 OR (L44 OR L45 OR L46 OR L47 OR
L59
            165
                L48) OR (L50 OR L51 OR L52) OR (L56 OR L57 OR L58)
                       (L44 OR L45 OR L46 OR L47) AND L59
L60
             83
                S
                       (L25 OR L26 OR L27 OR L28 OR L29) AND L60
             17
L61
                  S
                      (L25 OR L26 OR L27 OR L28 OR L29) AND L59
             41
                 S
L62
                      L59 AND ?CRYST?(4A)(SIZE## OR LARGE##### OR ENLARG##### OR DIMENSION#### OR
             28
                 s
L63
VOLUME### OR LENGTH### OR LONG#### OR ELONG##### OR NM OR MM)
             1 S
                       L37 AND L41
L64
                       L37 AND L48
L65
              0 S
                       L37 AND L49
L66
             2 S
            2 S
                      L37 AND (L50 OR L51 OR L52)
L67
            0 S
                      L37 AND (L56 OR L57 OR L58)
L68
            5 S
2 S
                      L37 AND (L61 OR L62 OR L63)
L69
                      L37 AND (L44 OR L45)
L70
           14 S
30 S
10 S
14 S
8 S
5 S
                      L41 AND (L44 OR L45)
L71
L72
                      L41 AND (L47 OR L48)
                      L41 AND (L50 OR L51 OR L52)
L73
                      L71 AND L72
L74
                      L71 AND L73
L75
```

L50 AND L51

L76

```
CAS/STN FILE 'REGISTRY' ENTERED AT 08:52:01 ON 17 SEP 2004
                      ("VINYLENE CARBONATE"/CN OR "VINYLENE CARBONATE POLYMER"/CN)
L1
                      "1,3-DIOXOLAN-2-ONE"/CN
L2
             1
                 S
             1 S
                      L2 NOT L1
L3
             1 S
                      GRAPHITE/CN
L4
                      CARBON/CN
L5
             1
    FILE 'WPIX' ENTERED
                      (US5352548 OR US20030134201 OR JP2002025612)/PN OR JP2002-0285154/PRN, AP OR
                S
             5
JP10284081/PN OR JP2001052737/PN
               SEL PLU=ON L6 1- IC:
                                           8 TERMS
L7
     FILE 'HCAPLUS' ENTERED
                      (US5352548 OR US20030134201 OR JP2002025612)/PN OR JP2002-0285154/PRN, AP OR
L8
              5 S
JP10284081/PN OR JP2001052737/PN
               SEL PLU=ON L8 1- IC :
                                            5 TERMS
L9
L10
          25804
                S
                      L7
          21182
                S
L11
                      (L10 OR L11) AND (L4 OR GRAPHIT## OR
                S
           5523
L12
               CRYST########### (2A) CARBONAC? OR L5(L) (CRYST########### OR MOONOCRYST########))
                      (("SECONDARY BATTERIES"/CT OR "BATTERIES, SECONDARY"/CT OR "STORAGE
BATTERIES"/CT) OR "SECONDARY BATTERY SEPARATORS"/CT OR "ELECTROLYTIC CELLS"/CT OR (RECHARG##### OR
SECONDARY) (2A) (CELL OR FUELCELL OR BATTERY)) AND (L4 OR GRAPHIT## OR CRYST##########(2A) CARBONAC? OR
L5(L)(CRYST############ OR MONOCRYST########))
           672 S NEGATIVE AND POSITIVE AND ELECTRODE AND (L4 OR GRAPHIT## OR
L14
CRYST########## (2A) CARBONAC? OR L5(L) (CRYST########## OR MONOCRYST########))
                      NEGATIVE ELECTRODE AND (L4 OR GRAPHIT## OR CRYST##########(2A)CARBONAC? OR
           834 S
L15
L5(L)(CRYST############ OR MONOCRYST########))
                      ANODE AND CATHODE AND NEGATIVE AND (L4 OR GRAPHIT## OR
            307 S
L16
CRYST########### (2A) CARBONAC? OR L5(L) (CRYST########## OR MONOCRYST########))
                      ANODE AND CATHODE AND POSITIVE## AND (L4 OR GRAPHIT## OR
L17
            367 S
CRYST########## (2A) CARBONAC? OR L5(L) (CRYST########### OR MONOCRYST########))
            308 S ANODE AND CATHODE AND NEGATIVE## AND (L4 OR GRAPHIT## OR
CRYST########## (2A) CARBONAC? OR L5(L) (CRYST########## OR MONOCRYST########))
                      NEGATIVE## AND POSITIVE## AND ELECTRODE AND (L4 OR GRAPHIT## OR
           673 S
L19
CRYST########## (2A) CARBONAC? OR L5(L) (CRYST########### OR MONOCRYST########))
                      (L12 OR L13 OR L14 OR L15 OR L16 OR L17 OR L18 OR L19) AND ((ORGANIC OR
SOLUTION OR SOLVENT OR SOLUTE OR SOLUTION OR LIQUID OR FLUID OR ELECTROLYTIC#########) OR
ORGANIC (3A) (SOLVENT OR SOLUTE OR SOLUTION OR DISSOL######) OR NONAQ######## OR NON(W) (AQ OR AQUEOUS))
                       (L10 OR L11) AND ((ORGANIC OR SOLUTION OR SOLVENT OR SOLUTE OR SOLUTION OR
          13645 S
LIQUID OR FLUID OR ELECTROLYTIC######### OR ORGANIC(3A)(SOLVENT OR SOLUTE OR SOLUTION OR
DISSOL######) OR NONAQ######## OR NON(W)(AQ OR AQUEOUS))
                       (L14 OR L15 OR L16 OR L17 OR L18 OR L19)
L22
           1356 S
                      L22 AND (LIQUID OR FLUID OR SOLUTION OR ELECTROLYTE OR ELECTROLY########)
                S
L23
            957
                      L21 AND (LIQUID OR FLUID OR SOLUTION OR ELECTROLYTE OR ELECTROLY#######)
                S
L24
          11820
                      LARG##### (3A) CRYST##########
                S
L25
          25298
                      LARG##### (3A) MONOCRYST##########
            227
L26
                      (CRYST######### OR MONOCRYST#########) (4A) (DIMENSION###### OR VOLUME OR
                S
          86078
L27
SIZE## OR SIZING OR SPACING OR LENGTH OR HEIGHT OR LONG#####)
                      (CRYST######### OR MONOCRYST########) (4A) (700 OR 750 OR 800 OR 850 OR 900 OR
          68294 S
L28
950 OR 1000 OR MM OR NM OR 70 OR 75 OR 80 OR 85 OR 90 OR 95 OR 100 OR 71 OR 69 OR 72 OR 73 OR 74)
          10316 S (HIGH### OR WELL###) (2A) (CRYST######### OR MONOCRYST######## OR ORDER########)
AND (L12 OR L13 OR L14 OR L15 OR L16 OR L17 OR L18 OR L19 OR L20 OR L21 OR L22 OR L23 OR L24 OR L25 OR
L26 OR L27 OR L28)
     FILE 'REGISTRY' ENTERED
L30
             30
                 S
                       LI/MF
```

FILE 'HCAPLUS' ENTERED

L31 18180 S (L12 OR L13 OR L14 OR L15 OR L16 OR L17 OR L18 OR L19 OR L20 OR L21 OR L22 OR L23 OR L24 OR L25 OR L26 OR L27 OR L28 OR L29) AND (L30 OR L1 OR LITHI#### OR L12 OR L13)

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Advanced Search: INSPEC - 1969 to date (INZZ)

Search history:

No.	Database	Search term	Info added since	Results	
1	INZZ	wada-\$.AU. AND solin-\$.AU.	unrestricted	12	show titles
2	INZZ	pure NEAR graphite	unrestricted	484	show titles
3	INZZ	2 AND crystal\$6 NEAR graphite	unrestricted	23	show titles
4	INZZ	graphite.DE. AND diffraction.DE. AND raman.DE. AND ray.DE.	unrestricted	85	show titles
5	INZZ	4 AND (cryst\$8 OR polycryst\$8 OR monocryst\$8)	unrestricted	47	show titles
6	INZZ	graphite AND '1350' AND '1580'	unrestricted	6	show titles
7	INZZ	graphite AND '1580' AND (cryst\$8 OR microcryst\$8 OR polycryst\$8 OR nanocryst\$8)	unrestricted	30	show titles
8	INZZ	7 AND (battery OR batteries OR fuel OR cell OR cells OR li OR lithium)	unrestricted	4	show titles

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Enter your search term(s): Search	tips	
	whole document	
Information added since:	or: none	Seat

(YYYYMMDD)

Select special search terms from the following list(s):

- Classification codes A: Physics, 0-1
- Classification codes A: Physics, 2-3
- Classification codes A: Physics, 4-5
- Classification codes A: Physics, 6
- Classification codes A: Physics, 7
- Classification codes A: Physics, 8
- Classification codes A: Physics, 9
- Classification codes B: Electrical & Electronics, 0-5

graphite

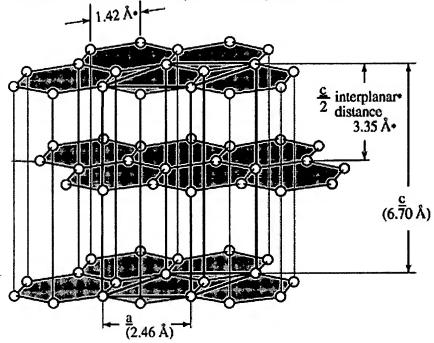
black lead; plumbago CAS: 7440-44-0

The crystalline allotropic form of carbon.

Occurrence: Naturally in Madagascar, Ceylon, Mexico, Korea, Austria, the former U.S.S.R., and China. Also produced synthetically by heating petroleum coke to approximately 3000C in an electric resistance furnace. Approximately 70% used in U.S. is synthetic.

Properties: Relatively soft, greasy feel; steel-gray to black color with a metallic sheen. D 2.0–2.25 depending on origin. Apparent d of artificial graphite 1.5–1.8. High electrical and thermal conductivity, specific heat 0.17 at room temperature, 0.48 at 1500C, tensile strength 400–2000 psi, compressive strength usually approximately 2000–8000 psi. Coefficient of friction 0.1 microns. Resistant to oxidation and thermal shock. Sublimes at 3650C.

Grade: Powdered, flake, crystals, rods, plates, fibers.



Hexagonal form of graphite.

Hazard: (Powder, natural) Fire risk. TLV: 2 mg/m³, respirable dust.

Use: Crucibles, retorts, foundry facings, molds, lubricants, paints and coatings, boiler compounds, powder glazing, electrotyping, monochromator in x-ray diffraction analysis, fluorinated graphite polymers with fluorine-to-carbon ratios of 0.1–1.25, electrodes, bricks, chemical equipment, motor and generator brushes, seal rings, rocket nozzles, moderator in nuclear reactors, cathodes in electrolytic cells, pencils, fibers, self-lubricating bearings, intercalation compounds.

See carbon; graphite fiber; carbon, industrial.

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databases



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document 3 of 6 Order Document

INSPEC - 1969 to date (INZZ)

Accession number & update

6426370, A2000-02-6865-028; 19991201.

Effe

Title

Effect of graphite crystal structure on lithium electrochemical intercalation.

Author(s)

Guerin-K; Fevrier-Bouvier-A; Flandrois-S; Couzi-M; Simon-B; Biensau-P.

Author affiliation

Centre de Recherche Paul Pascal, CNRS, Pessac, France.

Source

Journal-of-the-Electrochemical-Society (USA), vol.146, no.10, p.3660-5, Oct. 1999. , Published: Electrochem. Soc.

CODEN

JESOAN.

ISSN

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Availability

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Publication year 1999.

Language EN.

Publication type

J Journal Paper.

Treatment codes

P Practical; X Experimental.

Abstract

The electrochemical intercalation of lithium into various **graphite** materials has been examined in LiPF/sub 6/ solutions of ethylene carbonate (EC)/dimethyl carbonate (DMC) or EC/DMC/propylene carbonate (PC). When the **graphite** powder samples contained at least 30% of the rhombohedral form, no exfoliation was observed, even with electrolytes containing a large amount (80%) of PC. However, when the graphites were heat-treated at temperatures above 1000 degrees C, the faradaic losses due to the exfoliation reappeared, even though the rhombohedral phase content was unchanged. From Raman spectroscopy measurements, a correlation was found between the irreversible capacity due to the exfoliation and the ratio, R, of the integrated intensity of the disorder-induced line at **1350** cm/sup -1/ to the Raman-allowed line at **1580** cm/sup -1/. This suggests that structure defects, probably localized in

grain boundaries between rhombohedral and hexagonal domains, hinder the layer opening necessary for the intercalation of solvated lithium species at the beginning of the first electrochemical cycle. (23 refs).

Descriptors

<u>crystal-structure</u>; <u>electrochemistry</u>; <u>grain-boundaries</u>; <u>graphite-intercalation-compounds</u>; <u>lithium-compounds</u>; <u>Raman-spectra</u>.

Keywords

graphite crystal structure; Li electrochemical intercalation; LiPF6 solutions; ethylene carbonate; dimethyl carbonate; propylene carbonate; rhombohedral; exfoliation; faradaic losses; Raman spectroscopy; irreversible capacity; structure defects; grain boundaries; intercalation; first electrochemical cycle; **1350** to **1580** cm 1; Li C.

Classification codes

A6865 (Low-dimensional structures: growth, structure and

nonelectronic properties).

A8245 (Electrochemistry and electrophoresis).

A7830G (Infrared and Raman spectra in inorganic crystals).

A6170N (Grain and twin boundaries).

Chemical indexing

LiC bin, Li bin, C bin.

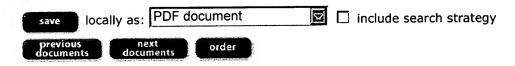
Numerical indexing

wavelength: 6.33E-06 to 7.41E-06 m.

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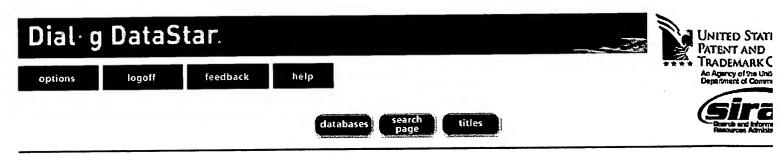
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document 4 of 47 Order Document

INSPEC - 1969 to date (INZZ)

Accession number & update

7806991, A2004-02-8630F-103, B2004-01-8410E-132; 20031201.

Title

The role of graphite surface group chemistry on graphite exfoliation during electrochemical lithium insertion.

Author(s)

Spahr-M-E; Wilhelm-H; Palladino-T; Dupont-Pavlovsky-N; Goers-D; Joho-F; Novak-P.

Author affiliation

TIMCAL SA, Bodio, Switzerland.

Source

11th International Meeting on Lithium Batteries, Monterey, CA, USA, 22-28 June 2002.

In: Journal-of-Power-Sources (Switzerland), vol.119-121, p.543-9, 1 June 2003.

CODEN

JPSODZ.

ISSN

ISSN: 0378-7753, CCCC: 0378-7753/03/ (\$30.00).

Availability

SICI: 0378-7753(20030601)119/121L.543:RGSG; 1-P.

Publication year

2003.

Language

EÑ.

Publication type

CPP Conference Paper, J Journal Paper.

Treatment codes

X Experimental.

Abstract

Heat treatment of highly **crystalline graphite** TIMREX(R) SLX50 at temperatures above 1200 degrees C in an inert gas atmosphere resulted in a significant increase of the irreversible capacity, which is observed during the first electrochemical lithium insertion using a 1M LiPF/sub 6/ ethylene carbonate/dimethyl carbonate 1:1 (w/w) electrolyte mixture. An additional potential plateau could be observed at about 0.45 V versus Li/Li/sup +/ during the galvanostatic insertion of lithium into these heat-treated **graphite** materials. Post-mortem scanning electron microscope studies of negative electrodes containing such heat-treated **graphite** materials indicated the exfoliation of the **graphite** structure as reason for the additional potential plateau and the significant increase of the irreversible capacity in the first electrochemical lithium insertion. The **graphite** exfoliation during the first electrochemical lithium

insertion disappeared when the heat-treated **graphite** materials were aged in a humid air atmosphere at room temperature for several months. This aging process turned out to be reversible. When regenerating the aged **graphite** material in a dry flux of argon gas at room temperature, the electrochemical **graphite** exfoliation could be observed again. Structure characterization of the **graphite** materials by **X-ray diffraction** (XRD) as well as surface investigations using **Raman** spectroscopy and gas absorption measurements indicated that the exfoliation tendency of **polycrystalline**, highly **crystallized graphite** in ethylene carbonate containing electrolytes in controlled neither by the rhombohedral stacking faults in the **graphite** structure, the surface defects, nor by the superficial disordered carbon but only by the surface group chemistry. The amount of acidic surface oxide groups especially seems to be the keys factor that influences **graphite** exfoliation during electrochemical lithium insertion in ethylene carbonate containing electrolytes. (38 refs).

Descriptors

ageing; anodes; argon; graphite; graphitisation; heat-treatment;

lithium; Raman-spectroscopy; secondary-cells; surface-chemistry; X- ray-diffraction.

Kevwords

graphite surface group chemistry; graphite exfoliation; electrochemical lithium insertion; heat treatment; highly crystalline graphite TIMREX R SLX50; inert gas atmosphere; ethylene carbonate dimethyl carbonate; electrolyte mixture; galvanostatic insertion; heat treated graphite materials; postmortem scanning electron microscope; negative electrodes; aging process; dry flux; argon gas; XRD; X ray diffraction; surface investigation; Raman spectroscopy; gas absorption measurement; polycrystalline; crystallized graphite; acidic surface oxide groups; 0.45 V; Li.

Classification codes

A8630F	(Secondary cells).
A8265	(Surface chemistry).
A8245	(Electrochemistry and electrophoresis).
A8140G	(Other heat and thermomechanical treatments).
B8410E	(Secondary cells).

Chemical indexing

Li int, Li el.

Numerical indexing

voltage: 4.5E-01 V.

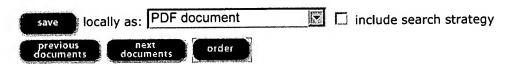
Copyright statement

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Digital object identifier

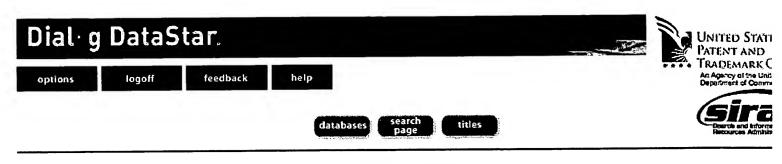
http://dx.doi.org/10.1016/S0378-7753(03)00284-2.

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document 3 of 47 Order Document

INSPEC - 1969 to date (INZZ)

Accession number & update

7819218, A2004-03-7830-007; 20040101.

Title

Raman spectroscopic and structural studies of heat-treated graphites for lithium-ion batteries.

Author(s)

Goers-D; Buga-H; Hardwick-L; Wursig-A; Novak-P.

Author affiliation

Lab for Electrochem, Paul Scherrer Inst, Villigen, Switzerland.

Source

Ionics (Germany), vol.9, no.3-4, p.258-65, 2003., Published: Inst. Ionics.

CODEN

IONIFA.

ISSN

ISSN: 0947-7047.

Availability

SICI: 0947-7047(2003)9:3/4L.258:RSSS; 1-N.

Publication year

2003.

Language

EN.

Publication type

J Journal Paper.

Treatment codes

X Experimental.

Abstract

Standard graphite TIMREX/sup (R)/ SLX 50 was oxidised at 500-800 degrees C under air atmosphere in a muffle and a rotary furnace. Scanning Electron Microscopy (SEM), Raman spectroscopy, and X-Ray Powder Diffraction (XRD) were used to study the changes in surface morphology and crystallinity. The results show a slight increase of the L/sub a/ value and a decrease of the rhombohedral fraction with increased heat-treatment temperature (HTT). XRD measurements show no significant change in L/sub a/ values within the bulk of graphite samples. Above 700 degrees C SEM images of graphite reveals holes and cavities, whereas heat-treatment temperatures below 700 degrees C do not significantly affect graphite materials parameters. (35 refs).

Descriptors

graphite; heat-treatment; oxidation; Raman-spectra; scanning-electron-microscopy; surface-morphology; X-ray-

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document 3 of 4 Order Document

INSPEC - 1969 to date (INZZ)

Accession number & update

5475592, A9704-7830-031; 970122.

Title

Characterization of polyparaphenylene (PPP)-based carbons.

Author(s)

Matthews-M-J; Dresselhaus-M-S; Endo-M; Sasabe-Y; Takahashi-T; Takeuchi-K.

Author affiliation

Dept of Phys, MIT, Cambridge, MA, USA.

Source

Journal-of-Materials-Research (USA), vol.11, no.12, p.3099-109, Dec. 1996., Published: Mater. Res. Soc.

CODEN

JMREEE.

ISSN

ISSN: 0884-2914, CCCC: 0884-2914/96/ (\$2.50).

Availability

SICI: 0884-2914(199612)11:12L.3099:CPBC; 1-8.

Publication year

1996.

Language

EN.

Publication type

J Journal Paper.

Treatment codes

X Experimental.

Abstract

Polyparaphenylene (PPP)-based carbons heat-treated at temperatures (T /sub HT/) from 600 degrees C up to 3000 degrees C have been characterized both structurally and in terms of their physical properties. Special attention is given to PPP heat treated at 700 degrees C (denoted by PPP-700), since samples heat-treated to this temperature were observed to have exceptionally high lithium affinities when electrochemically doped with Li. At low T/sub HT/ below 700 degrees C, it is found that the local structure of PPP-based samples can be characterized mostly in terms of a disordered polymer. As a result of heat treatment to high temperature, PPP-based carbon shows graphitization behavior with regard to X-ray diffraction d/sub 002/ (graphite c-axis d-spacing) development and to the increase of the Raman I/sub G//I/sub D/ intensity ratio (where I/sub G/ and I/sub D/ are the integrated intensities of the 1580 cm/sup -1/ and 1360 cm /sup -1/ Raman modes, respectively), as is found in so-called graphitizing carbons.

However, development of the c-axis **crystallite** size (L/sub c/) is restricted to very small values, in the range of so-called nongraphitizing carbons, while the a-axis **crystallite** size (L/sub a/) attains values up to roughly 120 AA for heat treatments near 3000 degrees C. These structural properties of PPP-based carbons are consistent with the observed electrical characteristics and their dependence on T/sub HT/. (22 refs).

Descriptors

carbon; graphitisation; heat-treatment; high-temperature-effects;

<u>magnetic-susceptibility</u>; <u>particle-size</u>; <u>Raman-spectra</u>; <u>scanning-electron-microscopy</u>; <u>secondary-cells</u>; <u>transmission-electron-microscopy</u>; <u>X-ray-diffraction</u>.

Keywords

Raman spectra; secondary **battery** applications; polyparaphenylene based C; high temperature heat treatment; c axis **crystallite** size; nongraphitizing C; electrical characteristics; **crystallite** size; 600 to 3000 C; **1580** cm 1; 1360 cm 1: C.

Classification codes

A7830L (Infrared and Raman spectra in disordered solids).

A7530C (Magnetic moments and susceptibility in magnetically ordered materials).

A8140G (Other heat and thermomechanical treatments).

Chemical indexing

C el.

Numerical indexing

temperature: 8.73E+02 to 3.27E+03 K; wavelength: 6.33E-06 m, 7.35E-06 m.

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document 16 of 47 Order Document

INSPEC - 1969 to date (INZZ)

Accession number & update

7249412, A2002-11-7920D-005; 20020429.

Title

Highly oriented graphite layer obtained on WC-Co by laser modification.

Author(s)

Ohkawara-Y; Shinada-T; Ohshio-S; Hiraga-H; Inoue-T; Saitoh-H.

Author affiliation

Dept of Chem, Nagaoka Univ of Technol, Niigata, Japan.

Source

Japanese-Journal-of-Applied-Physics-Part-2 (Letters)(Japan), vol.41, no.2A, p.L158-60, 1 Feb. 2002. , Published: Japan Soc. Appl. Phys.

CODEN

JAPLD8.

ISSN

ISSN: 0021-4922.

Availability

SICI: 0021-4922(20020201)41:2AL.I158:HOGL; 1-#.

Publication year

2002.

Language

EN.

Publication type

J Journal Paper.

Treatment codes

X Experimental.

Abstract

The surface of tungsten carbide sintered with cobalt binder (WC-Co) was modified by one pulse of 5 ms irradiation using an Nd:YAG laser in argon, carbon dioxide and air atmospheres. At the irradiated area on the surface of the sample, the color of the surface was completely different from that of the nonirradiated area, with the occurrence of 40 mu m surface swelling. In addition, Raman spectra indicated a very sharp and intense peak at 1580 cm/sup -1/, suggesting the presence of well-crystallized graphite. X-ray diffractometry revealed the existence of clear (002), (004) and (006) diffraction lines which are attributable to graphite. (9 refs).

Descriptors

ceramics; cobalt; graphite; laser-beam-effects; Raman-spectra;











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document 41 of 47 Order Document

INSPEC - 1969 to date (INZZ)

Accession number & update

4316772, A9304-2852-028; 930108.

Title

On the characterization of graphite.

Author(s)

Tanabe-T; Niwase-K; Tsukuda-N; Kuramoto-E.

Author affiliation

Fac of Eng, Osaka Univ, Japan.

Source

Fifth International Conference on Fusion Reactor Materials (ICFRM-5), Clearwater, FL, USA, 17-22 Nov. 1991.

Sponsors: Miner. Metals and Mater. Soc., ASM Int., Atomic Energy Soc. Japan.

In: Journal-of-Nuclear-Materials (Netherlands), vol.191-194, pt.A, p.330-4, Sept. 1992.

CODEN

JNUMAM.

ISSN IS

ISSN: 0022-3115, CCCC: 0022-3115/92/ (\$05.00).

Publication year

1992.

Language

EN.
Publication type

CPP Conference Paper, J Journal Paper.

Treatment codes

X Experimental.

Abstract

The authors have tried to make a new characterization of **graphite** from a aspect of lattice ordering in directions both parallel and perpendicular to the basal plane by means of laser **Raman** spectroscopy, **X-ray diffraction**, positron annihilation and transmission electron microscopy (TEM). The **Raman** technique is found to give information on the defects both at intra- and inter-basal planes, and disordering of the basal planes. **X-ray diffraction** easily see the disordering, but not the defects in the basal plane. And positron annihilation is very sensitive to the point defect in the basal plane which is not so easy to be detected even in high resolution TEM. The results obtained with the present techniques are compared to material properties like electrical conductivity and outgassing to extract useful correlations between them. (21 refs).

Descriptors





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document 1 of 6 Order Document

INSPEC - 1969 to date (INZZ)

Accession number & update

7619061, A2003-12-8115I-069, B2003-06-0520X-035; 20030520.

Title

SEM and Raman investigation of RF plasma assisted pulsed laser deposited carbon films.

Author(s)

Cappelli-E; Orlando-S; Mattei-G; Zoffoli-S; Ascarelli-P.

Author affiliation

IMAI, CNR, Rome, Italy.

Source

Applied-Surface-Science (Netherlands), vol.197-198, p.452-7, 30 Sept. 2002. , Published: Elsevier.

CODEN

ASUSEE.

ISSN

ISSN: 0169-4332, CCCC: 0169-4332/2002/ (\$22.00).

Availability

SICI: 0169-4332(20020930)197/198L.452:RIPA; 1-7

Electronic Journal Document Number: S0169-4332(02)00362-8.

Publication year

2002.

Language

EN.

Publication type

J Journal Paper.

Treatment codes

X Experimental.

Abstract

Thin carbon films with different percentages of sp/sup 3/ and sp/sup 2 / configurations, obtained by different deposition methods, have been proved to have electron emission properties, when submitted to high electric fields. The field emission properties seem to be associated with the presence of conductive nano-structured **graphite** particles embedded in an insulating amorphous carbon matrix. A general feature of these films is the presence of well-separated Raman peaks at **1350** and **1580** cm/sup -1/. The aim of our research is to evaluate the influence of an ancillary radio frequency energy source, on the structure of carbon films, obtained by a **graphite** target ablation. The plasma activated method is compared to traditional pulsed laser deposition (PLD) (Nd:YAG, lambda =532 nm), working under the same experimental conditions, optimised to obtain nanoparticle deposition. The substrate



temperature varied from room temperature (RT) up to 1000 K, to evaluate the influence of thermal energy on the cluster condensation. The structure of the films grown at different conditions has been examined by scanning electron microscopy (SEM) analysis to determine the occurrence of nano-structured compounds. This information has been correlated to the data on film quality obtained by micro-Raman analysis. (24 refs).

Descriptors

amorphous-state; carbon; electron-field-emission; graphite; nanoparticles; plasma-deposition; pulsed-laser-deposition; Raman-spectra; scanning-electron-microscopy; thin-films.

Keywords

micro Raman analysis; SEM; scanning electron microscopy; RF plasma assisted pulsed laser deposition; sp3 configurations; sp2 configurations; electron emission properties; electric fields; field emission properties; conductive nano structured **graphite** particles; insulating amorphous carbon matrix; radio frequency energy source; carbon films structure; **graphite** target ablation; nanoparticle deposition; substrate temperature; room temperature; thermal energy; cluster condensation; nano structured compounds; 532 nm; **1580** cm 1; **1350** cm 1; 293 to 1000 K; C.

Classification codes

A8115I	(Pulsed laser deposition).
A6855	(Thin film growth, structure, and epitaxy).
A7830G	(Infrared and Raman spectra in inorganic crystals).
A6146	(Structure of solid clusters, nanoparticles, and
	nanostructured materials).
A7970	(Field emission and field ionization).
A5275R	(Plasma applications in manufacturing and materials
	processing).
A7865M	(Optical properties of amorphous and glassy semiconductors
	and insulators (thin films/low-dimensional structures)).
A7830L	(Infrared and Raman spectra in disordered solids).
B0520X	(Other thin film deposition techniques).

Chemical indexing

C el.

Numerical indexing

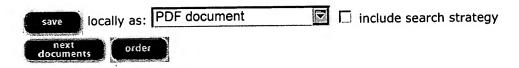
temperature: 2.93E+02 to 1.0E+03 K;

wavelength: 5.32E-07 m, 6.33E-06 m, 7.41E-06 m.

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L77 ANSWER 4 OF 47 HCAPLUS COPYRIGHT ACS on STN
                                      Entered STN: 02 Apr 2004
AN
     2004:269719 DN 140:290016 ED
     Nonaqueous electrolyte secondary battery
TΤ
     Yanagida, Katsunori; Inoue, Takao; Nakanishi, Naoya; Funahashi, Atsuhiro;
IN
     Nohma, Toshiyuki
     PATENT NO.
                                            APPLICATION NO.
                         KIND
                                DATE
                                            _____
                                _____
                         ____
                                                                   20030930
     US 2004062993
                                20040401
                                            US 2003-673350
                          A1
ΡI
                                            JP 2002-284740
                                                                   20020930
                         A2
                                20040415
     JP 2004119326
PRAI JP 2002-284740
                         A
                                20020930
     A nonaq. electrolyte secondary battery includes a pos. electrode, a neg. electrode comprising a
     graphite as a neg. electrode active material, and a nonaq. electrolyte including at least a
      saturated cyclic carbonic ester and containing a cyclic carbonic ester having a carbon-carbon
      double bond such that, when a content of the cyclic carbonic ester having a carbon-carbon double
      bond is x (g), a content of the graphite in the neg. electrode is B (g), a sp. surface area of
      the graphite is A (m2/g), a size of the crystallite of the graphite in a direction of the c axis
      is Lc, and a size of the crystallite of the graphite in a direction of the a axis is La, a
     condition expressed by: 0.05+10-2 \le x/[A + B + 2Lc/(2Lc+La)] \le 3+10-2 is satisfied.
     96-49-1, Ethylene carbonate 108-32-7, Propylene carbonate 872-36-6, Vinylene carbonate
     4437-85-8, Butylene carbonate 7782-42-5, Graphite, uses
        (nonaq. electrolyte secondary battery)
     96-49-1 HCAPLUS
RN
     1,3-Dioxolan-2-one (9CI) (CA INDEX NAME)
CN
RN
     108-32-7 HCAPLUS
     1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME)
CN
     872-36-6 HCAPLUS
     1,3-Dioxol-2-one (9CI) (CA INDEX NAME)
CN
     7782-42-5 HCAPLUS
RN
     Graphite (8CI, 9CI)
CN
                         (CA INDEX NAME)
     9004-32-4, Carboxymethyl cellulose sodium salt
IT
         (nonaq. electrolyte secondary battery)
     9004-32-4 HCAPLUS
RN
     Cellulose, carboxymethyl ether, sodium salt (8CI, 9CI) (CA INDEX NAME)
CN
     CM
          1
     CRN 9004-34-6
     CMF Unspecified
     CCI PMS, MAN
     STRUCTURE DIAGRAM IS NOT AVAILABLE ***
     CM
          2
     CRN 79-14-1
     CMF C2 H4 O3
  но_ С_ сн2_ он
      9003-55-8
 IT
         (styrene-butadiene rubber, nonaq.
         electrolyte secondary battery)
```

Benzene, ethenyl-, polymer with 1,3-butadiene (9CI) (CA INDEX NAME)

9003-55-8 HCAPLUS

RN

CN

L77 ANSWER 5 OF 47 HCAPLUS COPYRIGHT ACS on STN

AN 2004:201000 DN 140:238469

ED Entered STN: 12 Mar 2004

TI Anode material for secondary nonaqueous electrolyte battery

IN Dozono, Mitsuaki

PT

PRAI JP 2002-238055 20020819

The material comprises a 2 layer structured carbonaceous material: containing a graphite particle core, which is obtained by mech. milling with classification and has average particle size 10-40 µm, spec. surface area ≤10 m2/g, x-ray diffraction d(002) lattice spacing <0.337nm, c-axis crystallite size Lc ≥ 100 nm, true sp. gr. 2.18-2.25, tapping d. 1.0-1.3, I1360/I1580 ≥0.5 (I1360 and I1580 are the intensities of peaks at 1360 and 1580/cm on its Ar laser Raman spectrum), and 1580 cm-1 half width ≥26 cm-1; and a carbonaceous matter coating layer, obtained by coating a C precursor on the core surface followed by heat treating in an inner atmospheric at 800-2800°.

IT 7782-42-5, Graphite, uses

(anodes containing two layer structured carbonaceous materials with controlled characteristics for **secondary** lithium **batteries**)

RN 7782-42-5 HCAPLUS

CN Graphite (8CI, 9CI) (CA INDEX NAME)

```
L77 ANSWER 8 OF 47 HCAPLUS COPYRIGHT ACS on STN
    2003:929455 DN 139:384030 ED Entered STN: 28 Nov 2003
ΔN
ΤI
    Nonaqueous electrolyte secondary battery
     Shoji, Masashi; Igaki, Emiko; Tanahashi, Masakazu; Nakamura, Toshikazu;
IN
     Shimada, Mikinari
     Matsushita Electric Industrial Co., Ltd., Japan
PA
                                         APPLICATION NO.
                                                                  DATE
     PATENT NO.
                       KIND
                               DATE
                               _____
                               20031126 EP 2003-11623
                                                                  20030522
    EP 1365460
                        A2
ΡI
                               20031127 US 2003-442397
    US 2003219649
                       A1
                                                                  20030521
                                                                  20030522
                         A2
                               20040402 JP 2003-145345
     JP 2004103554
                                                                  20030523
                                         CN 2003-136677
                        A
                               20031203
     CN 1459878
PRAI JP 2002-151449
                        A
                               20020524
     A nonaq. electrolyte secondary battery includes a battery case that is not corroded easily even
     at the time of over-discharging. The nonaq. electrolyte secondary battery includes a battery
     case serving as a neg. electrode terminal, and a pos. electrode, a neg. electrode, a separator
     and a nonaq. electrolyte that are enclosed in the battery case. The pos. electrode and the neg.
     electrode resp. include an active material that stores and releases lithium reversibly. The
     battery case includes a case formed of a metal plate having iron as a principal component and a
     metal layer formed at least in a part of an inner surface of the case, and the metal layer
     includes a metallic element that dissolves in the nonaq. electrolyte at a lower potential than
     iron and at a higher potential than lithium.
     96-49-1, Ethylene carbonate 7782-42-5, Graphite
IT
        (nonaq: electrolyte secondary battery)
     96-49-1 HCAPLUS
RN
     1,3-Dioxolan-2-one (9CI) (CA INDEX NAME)
CN
     7782-42-5 HCAPLUS
RN
     Graphite (8CI, 9CI) (CA INDEX NAME)
CN
     9004-32-4, Cmc sodium salt
IT
        (nonaq. electrolyte secondary battery)
     9004-32-4 HCAPLUS
RN
     Cellulose, carboxymethyl ether, sodium salt (8CI, 9CI) (CA INDEX NAME)
CN
     CM
     CRN 9004-34-6
*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***
     CM
     CRN 79-14-1
     CMF C2 H4 O3
    _t__сн<sub>2</sub>__он
     9003-55-8
IT
        (styrene-butadiene rubber, nonaq. electrolyte secondary battery)
     9003-55-8 HCAPLUS
RN
     Benzene, ethenyl-, polymer with 1,3-butadiene (9CI) (CA INDEX NAME)
CN
     CRN 106-99-0
     CMF C4 H6
 H2C CH CH CH CH2
     CM
     CRN 100-42-5
     CMF C8 H8
```

H2C CH_Ph

L77 ANSWER 17 OF 47 HCAPLUS COPYRIGHT ACS on STN

AN 2003:260036 HCAPLUS Full-text

DN 138:274074

ED Entered STN: 04 Apr 2003

TI Battery anode active mass and its use in nonaqueous electrolyte battery

IN Inamasu, Tokuo; Yoshida, Hiroyuki; Nukuta, Toshiyuki; Nakagawa, Hiroe

PA Yuasa Corporation, Japan

PI JP 2003100294 A2 20030404 PRAI JP 2001-291637 20010925

The active mass is obtained by coating graphite containing ≥15% rhombohedral structure with a carbon material free of rhombohedral structure. Preferably, the graphite has crystallite size Lc .gtoreq.100 nm and the active mass has BET sp. surface area ≤3 m2/g for improved rate performance. The battery has an anode using the active mass, a cathode, and nonaq. electrolytes containing double bond-containing carbonates. Preferably, the electrolytes contain propylene carbonate for improved low-temperature performance. The battery has high energy d. and cycle performance owing to the active mass.

108-32-7, Propylene carbonate 872-36-6, Vinylene carbonate (nonaq. electrolyte containing; anode active mass of carbon-coated graphite for nonaq. battery

with high energy d. and cycle performance)

RN 108-32-7 HCAPLUS

CN 1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME)

$$0 \longrightarrow 0 \longrightarrow Me$$

IT

RN 872-36-6 HCAPLUS

CN 1,3-Dioxol-2-one (9CI) (CA INDEX NAME)

C

IT 7782-42-5, Graphite, uses

(rhombohedral structure-containing; anode active mass of carbon-coated graphite for nonaq. battery with high energy d. and cycle performance)

RN 7782-42-5 HCAPLUS

CN Graphite (8CI, 9CI) (CA INDEX NAME)

```
ANSWER 21 OF 47 HCAPLUS COPYRIGHT ACS on STN
L77
AN
     2001:648670 HCAPLUS Full-text
     135:360145
DN
     Entered STN: 05 Sep 2001
ΕD
     Structure, texture, and surface morphology modifications of highly crystalline graphite and the
ΤI
     consequences for its electrochemical lithium insertion behavior
     Spahr, Michael E.; Wilhelm, Henri; Joho, Felix; Novak, Petr
ΑIJ
     TIMCAL Group, Bodio, CH-6743, Switz.
CS
     ITE Letters on Batteries, New Technologies & Medicine (2001), 2(3),
SO
     B53-B58
     CODEN: ILBMF9
     ITE-IBA Publication Office
PB
DΤ
     Journal
     English
T.A
     52-2 (Electrochemical, Radiational, and Thermal Energy Technology)
CC
     Section cross-reference(s): 72
     The crystal structure, the texture, as well as the surface morphol. of the highly crystalline
AΒ
      synthetic graphite TIMREX SLX50 was modified by heat treatment under an inert gas atmospheric
     The heat-treated graphite showed a purely hexagonal crystal structure and a significantly lower
      specific BET surface area. Nitrogen adsorption measurements indicated a decreased amount of
     mesopores as well as a lower surface roughness of the graphite particles which accounts for the
     decrease in the specific BET surface area. The first electrochem. Li+ insertion in this heat-
     treated graphite indicated a strong exfoliation effect that led to a significant increase in the
      irreversible capacity. When the heat-treated graphite was subsequently oxidized in air at 800
      °C, its hexagonal crystal structure was preserved but no exfoliation occurred during the first
     Li+ insertion. Krypton adsorption measurements performed on TIMREX SLX50 before and after heat
      treatment indicated a surface curing effect. Both the amts. of prismatic surfaces (polar edges)
      and of low energy defects located on the graphite basal planes decrease as a result of the heat
      treatment. A progressive oxidation of this heat-treated hexagonal graphite tends to increase the
     number of prismatic surface defects but keeps the number of low energy defects unchanged. These
      results indicated that the decreased number of polar edges is responsible for the exfoliation of
      the graphite structure during the first electrochem. Li+ insertion. The rhombohedral stacking
      faults in graphite have no direct influence on its electrochem. performance. Nevertheless, they
      might control the number of surface defects and thus the tendency of highly crystalline graphite
      to exfoliate especially in propylene carbonate-containing electrolytes.
     108-32-7, 1,3-Dioxolan-2-one, 4-methyl-
TT
     7782-42-5, Graphite, uses
        (structure, texture, and surface morphol.
        modifications of highly crystalline graphite
        and the consequences for its electrochem. lithium insertion
```

behavior)
RN 108-32-7 HCAPLUS

CN 1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME)

С

RN 7782-42-5 HCAPLUS CN Graphite (8CI, 9CI) (CA INDEX NAME)

Jeff Harrison, 22511, JEF-4B68

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ANSWER 22 OF 47 HCAPLUS COPYRIGHT ACS on STN
L77
     2001:585538 HCAPLUS Full-text
AN
DN
     135:310105
     Entered STN: 14 Aug 2001
ED
     In situ SERS spectroscopy of Ag-modified pyrolytic graphite in organic electrolytes
ΤI
     Itoh, Takashi; Abe, Koji; Mohamedi, Mohamed; Nishizawa, Matsuhiko; Uchida, Isamu
ΑU
     Department of Applied Chemistry, Graduate School of Engineering, Tohoku
CS
     University, Sendai, 980-8579, Japan
     Journal of Solid State Electrochemistry (2001), 5(5), 328-333
SO
     CODEN: JSSEFS; ISSN: 1432-8488
PB
     Springer-Verlag
     Journal
DT
LA
     English
     73-3 (Optical, Electron, and Mass Spectroscopy and Other Related
CC
     Properties)
     Section cross-reference(s): 52, 72, 78
     Surface enhanced Raman scattering (SERS) was applied to study the Li
AB
     intercalation/deintercalation process at the interface of a pyrolytic graphite electrode with
     propylene and ethylene carbonate containing organic solns. The authors have focused on the
     lattice vibration of the most outer graphite surface layer simultaneously with cyclic
     voltammetric measurements. In situ Raman spectroscopy performed in this way allowed the authors
     to determine the La value that describes the size of graphitic microcrystallites along the a-
     axis. The La value decreases when the electrode is polarized to potentials between 0.02 and 1.0
     V. This phenomenon can be correlated with the intercalation of Li ions into the graphene
     structure. According to the spectral change, the size of the graphitic microcrystallites shows
     reversible behavior with potential cycling at the surface of the electrode.
     96-49-1, Ethylene carbonate 108-32-7, Propylene carbonate
IT
        (In situ SERS spectroscopy of Ag-modified pyrolytic graphite
        in organic electrolytes and lithium electrochem.
        intercalation and deintercalation)
     96-49-1 HCAPLUS
RN
     1,3-Dioxolan-2-one (9CI) (CA INDEX NAME)
CN
     108-32-7 HCAPLUS
RN
     1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME)
CN
     7439-93-2, Lithium, properties
IT
        (In situ SERS spectroscopy of Ag-modified pyrolytic graphite
        in organic electrolytes and lithium electrochem.
        intercalation and deintercalation)
     7439-93-2 HCAPLUS
RN
     Lithium (7CI, 8CI, 9CI) (CA INDEX NAME)
CN
 Li
     7782-42-5, Graphite, properties
IT
        (pyrolytic; In situ SERS spectroscopy of Ag-modified pyrolytic
        graphite in organic electrolytes and lithium
        electrochem. intercalation and deintercalation)
     7782-42-5 HCAPLUS
RN
     Graphite (8CI, 9CI) (CA INDEX NAME)
```

С

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L77 ANSWER 25 OF 47 HCAPLUS COPYRIGHT ACS on STN
    2000:672806 HCAPLUS Full-text
AN
DN
    133:269440
    Entered STN: 26 Sep 2000
ED
    Manufacture of carbon-coated graphite particles for
TΙ
    negative electrode in nonaqueous
     secondary battery
    Mitate, Takehito; Yamada, Kazuo
IN
PA
     Sharp Corp., Japan
                                                                 DATE
                                         APPLICATION NO.
     PATENT NO.
                        KIND DATE
                                           ______
                              _____
     ______
                        ----
                         A2
                               20000926
                                           JP 1999-77990
                                                                 19990323
     JP 2000264614
PΙ
PRAI JP 1999-77990
                               19990323
     Graphite particles are pre-treated with a sulfactant and sintered to give a carbon-coated
AB
     particles. The graphite particles have average face-to-face interval (d002) 0.335 -0.340Å
     determined by X-ray wide angular diffraction method, crystallite thickness (Lc) ≥10 nm on (002)
     direction and (La) \geq10 nm on (110) direction, BET sp. surface area 0.5-150 Nm2/g, and average
     particle diameter 0.7-80 µm. The carbon-coated graphite is used as neg. electrode in an nonaq.
     secondary battery using lithium-containing chalcogen chemical material such oxides as pos.
     electrode , and propylene carbonate or ethylene carbonate as electrolyte.
IT
     7782-42-5P, Graphite, uses
        (carbon-coated; manufacture of carbon-coated graphite particles
        for neg. electrode in nonaq.
        secondary battery)
RN
     7782-42-5 HCAPLUS
     Graphite (8CI, 9CI) (CA INDEX NAME)
CN
IT
     96-49-1, Ethylene carbonate 108-32-7, Propylene carbonate
        (electrolyte; manufacture of carbon-coated graphite
        particles for neg. electrode in nonaq.
        secondary battery containing)
RN
     96-49-1 HCAPLUS
     1,3-Dioxolan-2-one (9CI) (CA INDEX NAME)
CN
     108-32-7 HCAPLUS
RN
     1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME)
CN
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L77 ANSWER 27 OF 47 HCAPLUS COPYRIGHT ACS on STN
```

AN 2000:367147 HCAPLUS Full-text

DN 132:350274

ED Entered STN: 02 Jun 2000

TI Carbonaceous material for electrode and nonaqueous solvent secondary battery using this material

IN Kameda, Takashi; Ishihara, Tadashi

PA Mitsubishi Chemical Corporation, Japan

•••	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 1005097	A1	20000531	EP 1999-309419	19991125
	JP 2000223120	A2	20000811	JP 1999-16587	19990126
	JP 2000340232	A2	20001208	JP 1999-327768	19991118
JP 3534391	B2	20040607			
	US 6632569	B1	20031014	US 1999-447267	19991123
CN 1261729		A	20000802	CN 1999-127820	19991126
	TW 459416	В	20011011	TW 1999-88120711	19991126
	KR 2000035742	A	20000626	KR 1999-53275	19991127
PRAI	JP 1998-336796	A	19981127		
	JP 1999-80904	A	19990325		

AB A carbonaceous material has a plane space d002 of a (002) plane less than 0.337 nm in an X-ray wide angle diffraction method, a crystallite size (Lc) of 90 nm or higher, an R value, as a peak intensity ratio of a peak intensity of 1360 cm-1 to a peak intensity of 1580 cm-1 in a Raman spectrum in use of an argon ion laser, of 0.20 or higher, and a tap d. of 0.75 g/cm3 or higher. Also disclosed is a multilayer structure carbonaceous material for electrode, which is manufactured by carbonizing some organic compds. Where the carbonaceous material for electrode is mixed with the organic compds. The battery using the carbonaceous material for electrode or the multilayer structure carbonaceous material for electrode has a large capacity, a small irreversible capacity admitted in the initial cycle, excellent capacity maintaining rate of the cycle, and particularly, largely improved quick charging and discharging characteristics.

IT 7782-42-5, Graphite, uses

(carbonaceous material for electrode and nonaq.

solvent secondary battery using this

material)

RN 7782-42-5 HCAPLUS

CN Graphite (8CI, 9CI) (CA INDEX NAME)

IT 7439-93-2, Lithium, uses

(carbonaceous material for electrode and nonaq.

solvent secondary battery using this

material)

RN 7439-93-2 HCAPLUS

CN Lithium (7CI, 8CI, 9CI) (CA INDEX NAME)

IT 96-49-1, Ethylene carbonate

(carbonaceous material for electrode and nonag.

solvent secondary battery using this

material)

RN 96-49-1 HCAPLUS

CN 1,3-Dioxolan-2-one (9CI) (CA INDEX NAME)



```
L77 ANSWER 28 OF 47 HCAPLUS COPYRIGHT ACS on STN
AN
     1999:263263 HCAPLUS Full-text
DN
     130:340570
     Entered STN: 29 Apr 1999
ED
     Lithium intercalation into a plasma-enhanced-chemical-vapor-
ΤI
     deposited carbon film electrode
AII
     Pyun, Su-Il
     Department of Materials Science and Engineering, Korea Advanced Institute
CS
     of Science and Technology, Taejon, 305-701, S. Korea
SO
     Journal of the Korean Electrochemical Society (1999), 2(1), 38-45
     CODEN: JKESFC; ISSN: 1229-1935
     Korean Electrochemical Society
PB
DΤ
     Journal
LA
     English
     52-2 (Electrochemical, Radiational, and Thermal Energy Technology)
CC
```

Electrochem. lithium intercalation into a PECVD (plasma enhanced chemical vapor deposited) carbon film electrode was investigated in 1M LiPF6-EC (ethylene carbonate) and DEC (di-Et carbonate) solution during lithium intercalation and deintercalation, by using cyclic voltammetry supplemented with a.c.-impedance spectroscopy. The size of the graphitic crystallite in the a-and c-axis directions obtained from the carbon film electrode was much smaller than those of the graphite, indicating less-developed crystalline structure with hydrogen bonded to carbon, from the results of Auger electron spectroscopy, powder x-ray diffraction method, and FTIR spectroscopy. It was shown from the cyclic voltammograms and a.c.-impedance spectra of carbon film electrode that a threshold overpotential was needed to overcome an activation barrier to entrance of lithium into the carbon film electrode, such as the poor crystalline structure of the carbon film electrode showing disordered carbon and the presence of residual hydrogen in its structure. The exptl. results were discussed in terms of the effect of host carbon structure on the lithium intercalation capability.

Section cross-reference(s): 2



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7439-93-2, Lithium, reactions
(lithium intercalation into plasma-enhanced-chemical-vapor-deposited carbon film electrode)
RN 7439-93-2 HCAPLUS
CN Lithium (7CI, 8CI, 9CI) (CA INDEX NAME)
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Li

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ANSWER 30 OF 47 HCAPLUS COPYRIGHT ACS on STN
L77
     1998:478282 HCAPLUS Full-text
ΑN
DN
     129:138444
     Entered STN: 03 Aug 1998
ED
     Commercial cokes and graphites as anode materials for
ΤI
     lithium - ion cells
     Derwin, David J.; Kinoshita, Kim; Tran, Tri D.; Zaleski, Peter
ΑU
     Superior Graphite Co., Chicago, IL, 60638, USA
CS
     Materials Research Society Symposium Proceedings (1998), 496 (Materials for
SO
     Electrochemical Energy Storage and Conversion II--Batteries, Capacitors
     and Fuel Cells), 575-580
     CODEN: MRSPDH; ISSN: 0272-9172
PB
     Materials Research Society
DΤ
     Journal
LA
     English
     52-2 (Electrochemical, Radiational, and Thermal Energy Technology)
     Section cross-reference(s): 49
     Several types of carbonaceous materials from Superior Graphite Co. were investigated for lithium
AB
     ion intercalation. These com. available cokes, graphitized cokes and graphites have a wide range
     of phys. and chemical properties. The coke materials were investigated in propylene carbonate
     based electrolytes and the graphitic materials were studied in ethylene carbonate/di-Me solns. to
     prevent exfoliation. The reversible capacities of disordered cokes are below 230 mAh/g and those
     for many highly ordered synthetic (artificial) and natural graphites approached 372 mAh/g (LiC6).
     The irreversible capacity losses vary between 15 to as much as 200% of reversible capacities for
     various types of carbon. Heat treated cokes with the average particle size of 10 \mu showed marked
     improvements in reversible capacity for lithium intercalation. The electrochem. characteristics
     are correlated with data obtained from SEM, , high resolution transmission electron microscopy
     (TEM), x- ray diffraction and BET surface area anal. The electrochem. performance, availability,
     cost and manufacture ability of these com. carbons will be discussed.
IT
     96-49-1, 1,3-Dioxolan-2-one 108-32-7, 1,3-
     Dioxolan-2-one, 4-methyl- 7782-42-5, Graphite,
        (com. cokes and graphites as anode materials for
        lithium - ion cells)
     96-49-1 HCAPLUS
RN
     1,3-Dioxolan-2-one (9CI) (CA INDEX NAME)
CN
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RN 108-32-7 HCAPLUS CN 1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME)

RN 7782-42-5 HCAPLUS CN Graphite (8CI, 9CI) (CA INDEX NAME)

С

L77 ANSWER 31 OF 47 HCAPLUS COPYRIGHT ACS on STN

AN 1998:388450 HCAPLUS Full-text

DN 129:69918

ED Entered STN: 25 Jun 1998

TI Secondary nonaqueous-electrolyte lithium-ion

IN Ueda, Naoki; Ueshima, Hiroshi; Minato, Kazuaki; Mitate, Takehito; Yamada, Kazuo; Nishimura, Naoto

PA Denso Corp., Japan; Sharp K. K.

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
					-
PI	EP 847098	A1	19980610	EP 1997-120757	19971126
	EP 847098	B1	20020213		
	JP 10162858	A2	19980619	JP 1996-316457	19961127
	JP 3541913	B2	20040714		
	US 6027833	A	20000222	US 1997-979345	19971126
PRA	I JP 1996-316457	A	19961127		

The battery comprises ≥1 pair of electrodes and a separator provided between the electrodes and impregnated with a nonaq. electrolyte containing a mixed solvent of propylene carbonate and ethylene carbonate. At least 1 electrode of the at least 1 pair of electrodes has at least on surfaces of the electrodes an active substance layer made of composite C particles, which individually comprise a core of crystalline C and a low-crystallinity or amorphous C layer formed on at least a part of the surfaces of the core, and a C matrix covering at least a part of the composite C particles and uniformly dispersing and holding the composite C particles. When the active substance layer is subjected to the Raman spectroscopy using an Ar laser, a ratio of the peak intensity at 1350-1370/cm to a peak intensity at 1580-1620/cm is ≥0.4, and an average lattice spacing along the c axis in a graphite structure is 3.35-3.40 Å. The C matrix consists essentially of a carbonized product of a thermosetting resin, and the low-crystallinity or amorphous C layer is made of a carbonized deposit formed by thermally decomposing a gas-phase hydrocarbon on the core.

IT 7440-44-0, Carbon, uses

(lithium-ion battery anodes made of crystalline and low-crystallinity or amorphous)

RN 7440-44-0 HCAPLUS

CN Carbon (7CI, 8CI, 9CI) (CA INDEX NAME)

IT 108-32-7, Propylene carbonate

(lithium-ion battery electrolyte containing ethylene carbonate and)

RN 108-32-7 HCAPLUS

CN 1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME)

C

IT 96-49-1, Ethylene carbonate

(lithium-ion battery electrolyte containing propylene carbonate and)

RN 96-49-1 HCAPLUS

CN 1,3-Dioxolan-2-one (9CI) (CA INDEX NAME)

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L77 ANSWER 34 OF 47 HCAPLUS COPYRIGHT ACS on STN
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AN 1997:735851 HCAPLUS Full-text

DN 128:24926

ED Entered STN: 22 Nov 1997

TI Secondary lithium-ion battery

IN Fujimoto, Masahisa; Yoshinaga, Noriyuki; Ueno, Koji; Furukawa, Nobuhiro; Nohma, Toshiyuki; Takahashi, Masatoshi

PA Sanyo Electric Co., Ltd., Japan

SO U.S., 55 pp., Cont.-in-part of U.S. Ser. No. 48,063, abandoned. CODEN: USXXAM

DT Patent

LA English

IC ICM H01M010-40

NCL 429197000

CC 52-2 (Electrochemical, Radiational, and Thermal Energy Technology)

FAN.CNT 3

D. D. D. L. C.	TETATO	D 3 M D	ADDITCAMIAN	DATE
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5686138	A	19971111	US 1994-188609	19940124
US 5882818	A	19990316	US 1997-902337	19970729
บร 5993997	A	19991130	US 1998-49987	19980330
JP 1991-295835	A	19911112		
US 1992-850486	B1	19920312		
US 1993-48063	B 2	19930419		
US 1994-188609	A 3	19940124		
US 1997-902337	A3	19970729		
	US 5882818 US 5993997 JP 1991-295835 US 1992-850486 US 1993-48063 US 1994-188609	US 5686138 A US 5882818 A US 5993997 A JP 1991-295835 A US 1992-850486 B1 US 1993-48063 B2 US 1994-188609 A3	US 5686138 A 19971111 US 5882818 A 19990316 US 5993997 A 19991130 JP 1991-295835 A 19911112 US 1992-850486 B1 19920312 US 1993-48063 B2 19930419 US 1994-188609 A3 19940124	US 5686138 A 19971111 US 1994-188609 US 5882818 A 19990316 US 1997-902337 US 5993997 A 19991130 US 1998-49987 UP 1991-295835 A 19911112 US 1992-850486 B1 19920312 US 1993-48063 B2 19930419 US 1994-188609 A3 19940124

The battery comprises an anode composed mainly of a C material consisting essentially of a graphite having a d-value of the lattice plane (002) obtained by x-ray diffraction of 3.354-3.370, a crystallite size in the c-axis direction obtained by x-ray diffraction of 200 Å, an average particle diameter of 1-30 µm, a sp. surface area of 0.5-50 m2/g and a true d. of 1.9-2.25 g/cm3; a cathode composed mainly of a compound capable of intercalating and deintercalating Li and which is different from the graphite of the anode; a separator; and an electrolyte solution of an electrolyte solute dissolved in a solvent, the solvent comprising 20-80 volume% ethylene carbonate. The battery has a large capacity, small self-discharge rate and excellent cycle characteristics and high charge-discharge efficiency.

IT 7782-42-5, Graphite, uses

RL: DEV (Device component use); USES (Uses)
 (anodes in high-performance lithium-ion batteries)

RN 7782-42-5 HCAPLUS

CN Graphite (8CI, 9CI) (CA INDEX NAME)

IT 96-49-1, Ethylene carbonate 108-32-7, Propylene
 carbonate 4437-70-1, 2,3-Butylene carbonate 4437-85-8,
1,2-Butylene carbonate 20628-59-5, Ethylene thiocarbonate
 (in electrolytes of high-performance lithium-ion
 batteries)

RN 96-49-1 HCAPLUS

CN 1,3-Dioxolan-2-one (9CI) (CA INDEX NAME)

CN 1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME)

- L77 ANSWER 35 OF 47 HCAPLUS COPYRIGHT ACS on STN
- AN 1997:543494 HCAPLUS.Full-text
- DN 127:138099
- ED Entered STN: 27 Aug 1997
- TI Secondary nonaqueous-electrolyte battery
- IN Yamada, Kazuo; Mitate, Takehito; Nishimura, Naoto; Tsukuda, Yoshihiro; Minato, Kazuaki
- PA Sharp Kabushiki Kaisha, Japan

	01142 P 114244112114 -11				
	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
ΡI	EP 782207	A1	19970702	EP 1996-309540	19961224
	EP 782207	В1	20000816		
	JP 09237638	A2	19970909	JP 1996-326371	19961206
	JP 3481063	B2	20031222		
	US 6040092	A	20000321	US 1996-772255	19961223
PRAI	JP 1995-336697	A	19951225		
	JP 1996-326371	A	19961206		

The battery includes an anode of graphite particles coated with less crystallized C and a nonaq. electrolyte, which contains at least ethylene carbonate (EC) and propylene carbonate (PC). The interlayer spacing between the (002) planes of the graphite particles is 0.335-0.340 nm, the thickness of crystallite in the direction orthogonal to the (002) plane is ≥10 nm, and the thickness of crystallite in the direction orthogonal to the (110) plane is ≥10 nm. The graphite particles have ≤0.4 as the intensity ratio R of a peak in the vicinity of 1360 cm-1 relative to a peak in the vicinity of 1580 cm-1 in Ar lase Raman scattering, and R of the graphite particles coated with less crystallized C is >0.4. The wt.ratio of less crystallized C: (less crystallized C + graphite) is ≤20%. The volume ratio of PC: (PC + EC) = 0.1-0.5.

IT 7782-42-5, Graphite, uses

RL: DEV (Device component use); USES (Uses) (battery anodes from less crystallized carbon-coated particles of)

RN 7782-42-5 HCAPLUS

CN Graphite (8CI, 9CI) (CA INDEX NAME)

L77 ANSWER 36 OF 47 HCAPLUS COPYRIGHT ACS on STN

AN 1994:583569 HCAPLUS Full-text

DN 121:183569

ED Entered STN: 15 Oct 1994

TI Secondary nonaqueous electrolyte batteries with improved carbonaceous anodes and electrolyte solvents

IN Omaru, Atsuo; Nagamine, Masayuki; Date, Naoyuki

PA Sony Corp., Japan

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9414205	Al	19940623	WO 1993-JP1769	19931206
JP 06223878	A2	19940812	JP 1993-304366	19931203
EP 634805	A1	19950118	EP 1994-901040	19931206
EP 634805	в1	19980715		
US 5639575	A	19970617	US 1996-582047	19960102
AI JP 1992-325748		19921204		
WO 1993-JP1769		19931206		
US 1994-257000		19940729		
	JP 06223878 EP 634805 EP 634805 US 5639575 AI JP 1992-325748 WO 1993-JP1769	PATENT NO. KIND WO 9414205 A1 JP 06223878 A2 EP 634805 A1 EP 634805 B1 US 5639575 A AI JP 1992-325748 WO 1993-JP1769	PATENT NO. KIND DATE	PATENT NO. KIND DATE APPLICATION NO. WO 9414205 A1 19940623 WO 1993-JP1769 JP 06223878 A2 19940812 JP 1993-304366 EP 634805 A1 19950118 EP 1994-901040 EP 634805 B1 19980715 US 5639575 A 19970617 US 1996-582047 AI JP 1992-325748 19921204 WO 1993-JP1769 19931206

The batteries use anodes of a carbonaceous material having real d. ≥2.1 g/cm3, d002 <0.34 nm, crystallite thickness in c direction the 002 face >16.0 nm, and G value (peak strength at 1580 cm-1 of graphitic structure/peak strength at 1350 cm-1 of amorphous structure) ≥2.5 on its Raman spectrum; cathodes fo Li containing transition metal oxide having charge discharge capacity >250 mAh/unit weight of the carbonaceous material in the anode; and ethylene carbonate as electrolyte solvent. The solvent may also contain linear carbonate esters. These batteries have high energy d.

IT 7782-42-5, Graphite, uses

(natural and synthetic; secondary nonaq. electrolyte batteries with improved carbonaceous anodes and electrolyte solvents)

RN 7782-42-5 HCAPLUS

CN Graphite (8CI, 9CI) (CA INDEX NAME)

С

RN 96-49-1 HCAPLUS

CN 1,3-Dioxolan-2-one (9CI) (CA INDEX NAME)

```
L77
    ANSWER 40 OF 47 HCAPLUS COPYRIGHT ACS on STN
     1993:584774 HCAPLUS Full-text
AN
DN
     119:184774
     Entered STN: 30 Oct 1993
ED
TΙ
    Lithium secondary battery
     Fujimoto, Masahisa; Yoshinaga, Noriyuki; Ueno, Koji; Furukawa, Nobuhiro;
IN
     Nohma, Toshiyuki; Takahashi, Masatoshi
PA
     Sanyo Electric Co., Ltd., Japan
SO
     Eur. Pat. Appl., 60 pp.
     CODEN: EPXXDW
DT
     Patent
LA
    .English
    ICM H01M004-58
IC
     ICS H01M010-40
     52-2 (Electrochemical, Radiational, and Thermal Energy Technology)
CC
     Section cross-reference(s): 38
FAN.CNT 3
                                                                   DATE
                                            APPLICATION NO.
     PATENT NO.
                         KIND
                                DATE
     _____
                         ____
                                19930519
                                            EP 1992-103986
                                                                   19920309
PΙ
     EP 541889
                         A1
                         B1
                                19980909
     EP 541889
                                                                   19920402
                                19930513
                                            CA 1992-2064965
     CA 2064965
                         AA
                         С
                                19970603
     CA 2064965
PRAI JP 1991-295835
                         Α
                                19911112
                                19911203
     JP 1991-319200
                         Α
     JP 1991-325778
                                19911210
                          Α
     JP 1991-360254
                          Α
                                19911227
                                19901212
     JP 1990-401667
                          Α1
     The battery includes a cathode of a Li-intercalatable compound, an anode of a carbonaceous
AB
     material comprising mainly or only graphite, a separator, and an electrolyte of a Li salt in a
     solvent comprising \geq 1 cyclic compound such as ethylene carbonate, ethylene thiocarbonate, \gamma-
     thiobutyrolactone, \alpha-pyrrolidone, \gamma-butyrolactone, propylene carbonate, 1,2-butylene carbonate,
     etc. The graphite has an average particle diameter 1-30 μm, spacing of (002) planes 3.35-3.40 Å,
     crystallite size in c direction ≥150 Å, sp. surface area 0.5-50 m2/g, and true d. 1.9-2.3 g/cm3.
     The Li-intercalatable compound is LixMO2 or LiyM2O4, where M is a transition element, x≤1 and
     y≤2; metal oxide-, anion-, or halide-intercalated graphite; or a conductive polymer containing a
     dopant.
```

7782-42-5, Graphite, uses IT

(anodes, in high-performance organic-electrolyte lithium batteries)

RN 7782-42-5 HCAPLUS

Graphite (8CI, 9CI) (CA INDEX NAME) CN

96-49-1, 1,3-Dioxolan-2-one 108-32-7 4437-70-1, 2,3-Butylene carbonate 4437-85-8, IT 1,2-Butylene carbonate 20628-59-5, Ethylene thiocarbonate (electrolyte containing, for high-performance and long cycle-life lithium batteries)

RN 96-49-1 HCAPLUS

1,3-Dioxolan-2-one (9CI) (CA INDEX NAME) CN

108-32-7 HCAPLUS RN

1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME) CN

4437-70-1 HCAPLUS RN

1,3-Dioxolan-2-one, 4,5-dimethyl- (9CI) (CA INDEX NAME) CN

RN 4437-85-8 HCAPLUS

1,3-Dioxolan-2-one, 4-ethyl- (9CI) (CA INDEX NAME) CN

20628-59-5 HCAPLUS RN

1,3-Dioxolane-2-thione (9CI) (CA INDEX NAME) CN

L77 ANSWER 42 OF 47 HCAPLUS COPYRIGHT ACS on STN

AN 1993:216544 HCAPLUS Full-text

DN 118:216544

ED Entered STN: 29 May 1993

- TI Carbon anode for secondary lithium battery
- IN Tanaka, Hideaki; Mitate, Takehito; Kitayama, Hiroyuki; Yamada, Kazuo

PA Sharp Corp., Japan

PATENT NO. KIND DATE APPLICATION NO. D.	ATE
PI EP 520667 A1 19921230 EP 1992-305500 1	9920616
US 5344726 A 19940906 US 1993-79086 1	9930617
PRAI JP 1991-144547 A 19910617	
JP 1996-343196 A3 19910617	
US 1992-898804 B1 19920612	

The anode comprises a core of a highly crystalline C, which is covered with an amorphous C. The amorphous C has a turbostratic structure, an interlayer distance in the c-axis direction of 0.337-0.360 nm, and a peak ratio in Ar ion laser Raman spectra of 0.4:0.1 at a 1360 cm-1:1580 cm-1 ratio.

IT 7440-44-0P, Carbon, uses

(anodes from crystalline coated with amorphous carbon of turbostratic structure, preparation of, for lithium batteries)

RN 7440-44-0 HCAPLUS

CN Carbon (7CI, 8CI, 9CI) (CA INDEX NAME)

- L77 ANSWER 43 OF 47 HCAPLUS COPYRIGHT ACS on STN
- AN 1992:637175 HCAPLUS Full-text
- DN 117:237175
- ED Entered STN: 13 Dec 1992
- TI Lithium secondary battery and carbonaceous material used in this
- IN Takami, Norio; Ohsaki, Takahisa
- PA Toshiba Corp., Japan

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 495613	A2	19920722	EP 1992-300286	19920114
	EP 495613	. A3	19921216		
	EP 495613	B1	19980819		
	US 5244757	Α	19930914	US 1992-819224	19920113
PRAI	JP 1991-2859		19910114		
	JP 1991-110607		19910515		
	JP 1991-187999		19910729		
	JP 1991-213194		19910731		
	US 1992-819224		19920113		
	EP 1992-300286		19920114		

- The battery comprises a vessel containing a cathode, a Li+ ion-conducting electrolyte, and an anode of Li -intercalatable carbonaceous spherical particles or fibers. The carbonaceous spherical particles and fibers have the mean value of the spacing of (002) planes 0.337-0.380 nm, the mean size of the crystal lattice in the c-axis direction 1-25 nm, the H:C atomic ratio <0.15, and the Raman spectrum ratio R1:R2 0.5-1.5, where R1 and R2 are the resp. peak values at wave nos. 1360 and 1580 cm-1. The average size of the particles is 0.5-100 μm, and the resp. average diameter and length of the fibers are 1-100 and 1-200 μm. The preparation of particles and fibers includes carbonizing mesophase small spherical particles or mesophase pitch fibers in an inert gas or vacuum at >1200-2500°.
- IT 7439-93-2, Lithium, uses

(carbonaceous materials intercalatable with, anodes, for org
.-electrolyte batteries)

IT 96-49-1, Ethylene carbonate 108-32-7, Propylene carbonate

(electrolyte solvent mixts. containing, for lithium batteries)

- RN 96-49-1 HCAPLUS
- CN 1,3-Dioxolan-2-one (9CI) (CA INDEX NAME)
- RN 108-32-7 HCAPLUS
- CN 1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME)

```
L77 ANSWER 44 OF 47 HCAPLUS COPYRIGHT ACS on STN
     1990:162180 HCAPLUS Full-text
AN
DN
     112:162180
     Entered STN: 28 Apr 1990
ED
    Lithium secondary battery and electric
TI
     double layer capacitor using carbon fiber electrode
     Endo, M.; Okada, Y.; Nakamura, H.
ΑU
     Fac. Eng., Shinshu Univ., Nagano, 380, Japan
CS
     Synthetic Metals (1990), Volume Date 1989, 34(1-3), 739-44
SO
     CODEN: SYMEDZ; ISSN: 0379-6779
     Journal
DT
     English
LA
     52-2 (Electrochemical, Radiational, and Thermal Energy Technology)
CC
     Section cross-reference(s): 76
     The performance of secondary Li batteries was evaluated as a function of the crystallinity of C
ΔR
     fiber cathode materials, using LiClO4-propylene carbonate (I) as electrolyte. C fibers prepared
     by evaporation and with a well defined graphite-like structure performed best, with a stable
     discharge potential of .apprx.4.5 V vs. Li reference and a specific capacity of 270 C/g. A
     double layer capacitor with large surface area (300 m2/g) activated C fibers and LiClO4-I
     electrolyte had stable cycling behavior. The mechanism in both devices is attributed to
     electrochem. intercalation of Li+ and ClO4-.IT 7440-44-0
     7440-44-0
IT
        (carbon fibers, cathodes, lithium and perchlorate
        intercalation by, crystallinity and porosity effect on)
     7440-44-0 HCAPLUS
RN
     Carbon (7CI, 8CI, 9CI) (CA INDEX NAME)
CN
IT
     108-32-7, Propylene carbonate
        (electrolytes containing, carbon fiber cathode performance in, for
        lithium batteries and double-layer capacitors)
     108-32-7 HCAPLUS
RN
     1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME)
CN
     7439-93-2, Lithium, reactions
IT
        (intercalation of, by carbon fiber cathodes,
        crystallinity and pore size effect on)
     7439-93-2 HCAPLUS
RN
     Lithium (7CI, 8CI, 9CI) (CA INDEX NAME)
CN
```

Li

- L77 ANSWER 46 OF 47 HCAPLUS COPYRIGHT ACS on STN
- AN 1989:42059 HCAPLUS Full-text
- DN 110:42059
- ED Entered STN: 04 Feb 1989
- TI Secondary nonaqueous batteries with carbonaceous anode supports
- IN Sato, Yuichi; Inada, Kuniaki; Ikeda, Katsuharu; Nose, Hiroyoshi; Miyabayashi, Mitsutaka; Itsubo, Akira; Yui, Hiroshi; Komada, Megumi
- PA Toshiba Battery Co., Ltd., Japan; Mitsubishi Petrochemical Co., Ltd.
- SO Jpn. Kokai Tokkyo Koho, 8 pp.
 - CODEN: JKXXAF
- DT Patent
- LA Japanese
- IC ICM H01M004-02
 - ICS H01M004-58; H01M004-62
- CC 52-2 (Electrochemical, Radiational, and Thermal Energy Technology) Section cross-reference(s): 38

FAN. CNT 1

PATENT NO.		KIND	DATE	APPLICATION NO.	DATE
PI	JP 63193463	A2	19880810	JP 1987-22483	19870204
PRAT	JP 1987-22483		19870204		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
TD C21024C2	TCM	TIO1MOOA 02

JP 63193463 ICM H01M004-02

ICS H01M004-58; H01M004-62

The batteries have Li or Li-based anode-active mass loaded on particles of a carbonaceous AB material bonded by particles of a thermoplastic polyolefin. The carbonaceous material has a volume-average diameter d <100 μm, comprises crystalline and amorphous structural units, has a H:C atomic ratio r < 0.15, G < 2.5 where G is the ratio of the Raman spectrum peak area of the material at 1580 ±100/cm wave number to that at 1360 ±100/cm wave number using a 5145-Åwavelength Ar-laser light source, a spacing of (002) planes d' >3.37 Å, and a unit-cell length in its c-axial direction L <150 Å. The structural units may have d <200 Å, the polyolefin may have d less than 3 times that of the carbonaceous material, and the carbonaceous material has a sp. surface area A >1 m2/g. The polyolefin can be polyethylene, polypropylene, poly(1-butene), and copolymers of C2H4, C3H6, and/or α -olefins. Thus, Novolak resin (average mol. weight 2600) was heated at 1900° in N for 1 h and activated by heating at 800-900° for 2 h in a 0.5-g/g heattreated material/min steam flow to obtain a carbonaceous material having ${f r}={f 0.04},$ G = 0.60, d' = 3.60 Å, L = 15 , A = 15 m2/g, and d = 5 μ m. A 50-mg mixture containing 94% this material and 6% polyethylene (d = 0.5 time that of the carbonaceous material) was pressed to a 0.5-mm-thick pellet and loaded with 1.0-mA-h Li to obtain by electrolysis at 0.5 mA/cm2 in a 1M Li+ solution an anode. A battery using this anode, a 1M LiClO4/propylene carbonate electrolyte, and a cathode prepared from a mixture of V2O5 and (NH4)3PO4.3H2O and pre-loaded with 6.0-mA-h Li had a longer cycle life and smaller self discharge than a control battery.

```
L83 ANSWER 1 OF 7 HCAPLUS COPYRIGHT ACS on STN
AN
    2003:452214 HCAPLUS Full-text
DN
    139:24108
    Entered STN: 13 Jun 2003
ED
TΙ
    Secondary nonaqueous-electrolyte
    battery with anode containing carbon-coated graphite
    Koji, Yoshihiro; Inomata, Hideyuki; Takahashi, Masatoshi
IN
PA
    Sanyo Electric Co., Ltd., Japan
SO
    Jpn. Kokai Tokkyo Koho, 7 pp.
    CODEN: JKXXAF
DΤ
    Patent
I.A
    Japanese
TC
    ICM H01M004-58
    ICS H01M004-02; H01M010-40
CC
    52-2 (Electrochemical, Radiational, and Thermal Energy Technology)
FAN.CNT 1
                                         APPLICATION NO.
    PATENT NO.
                      KIND DATE
                       ____
                                          _____
     _____
PI JP 2003168429 A2
PRAI JP 2001-365167
                       A2 20030613 JP 2001-365167 20011129
                             20011129
CLASS
              CLASS PATENT FAMILY CLASSIFICATION CODES
 PATENT NO.
 JP 2003168429 ICM H01M004-58
                ICS H01M004-02; H01M010-40
     The claimed battery is equipped with an anode containing graphite particle having Lc value ≥150 Å
AB
     and d value ≤3.38 Å, which is coated with C having lower crystallinity than the graphite, where
     the coated graphite particle has 5145 A ar laser Raman spectrometry peak intensity at 1360 cm-1
     (I1360) and 1580 cm-1 (I1580) satisfying (I1360/I1580) 0.17-0.23 and 1580 cm-1 half width 19-28
     and the anode contains 1-10 weight parts (to the coated graphite particle) conductive C powder
     having sp. surface area \geq 10 m2/g. The battery provides high large current discharge capacity and
     long cycle life.
     7782-42-5, Graphite, uses
IT
        (secondary nonaq.-electrolyte
       battery with anode containing carbon-coated graphite
```

С

RN CN particle)
7782-42-5 HCAPLUS

Graphite (8CI, 9CI) (CA INDEX NAME)

```
Entered STN: 16 Aug 2002
ΕD
    Secondary nonaqueous electrolyte
TΙ
    battery and its manufacture
    Kajikawa, Satoshi; Ozaki, Yoshiyuki; Omori, Keisuke
ΤN
    Matsushita Electric Industrial Co., Ltd., Japan
PA
    Jpn. Kokai Tokkyo Koho, 7 pp.
SO
    CODEN: JKXXAF
DT
    Patent
LA
    Japanese
    ICM H01M010-40
IC
    ICS H01M010-40; H01M002-16; H01M004-02;
         H01M004-58; H01M004-62
    52-2 (Electrochemical, Radiational, and Thermal Energy Technology)
CC
FAN.CNT 1
                    KIND
                                        APPLICATION NO.
    PATENT NO.
                              DATE
                                        ______
                             _____
    _____
    JP 2002231316
                       A2 20020816
                                         JP 2001-21156
                                                             20010130
PRAI JP 2001-21156
                             20010130
CLASS
PATENT NO. CLASS PATENT FAMILY CLASSIFICATION CODES
JP 2002231316 ICM H01M010-40
               ICS H01M010-40; H01M002-16; H01M004-02;
                      H01M004-58; H01M004-62
     The battery has a Li containing transition metal oxide cathode, a Li intercalating carbonaceous
```

AB The battery has a Li containing transition metal oxide cathode, a Li intercalating carbonaceous anode, a separator, and a nonaq. electrolyte solution; where the carbonaceous material is a low crystallinity material with interplanar spacing d002 0.372-0.400 nm, the anode contains 2-6% (of the carbonaceous material) conductor having conductivity higher than the carbonaceous material, and the electrolyte soln. has a Li salt concn 0.7-0.9M. The battery is prepared by winding an electrode-separator stack, while applying a tensile stress to the electrodes and separator at 1 end, and pressing the stack with a roller.

IT 96-49-1, Ethylene carbonate

RL: DEV (Device component use); USES (Uses)
(electrolyte solns. with controlled lithium
salt concns. for secondary lithium
batteries)

L83 ANSWER 2 OF 7 HCAPLUS COPYRIGHT ACS on STN

2002:611897 HCAPLUS Full-text

RN 96-49-1 HCAPLUS

CN 1,3-Dioxolan-2-one (9CI) (CA INDEX NAME)



AN

DN

137:157187

- L83 ANSWER 3 OF 7 HCAPLUS COPYRIGHT ACS on STN
- AN 2002:464554 HCAPLUS Full-text
- DN 137:35516
- ED Entered STN: 21 Jun 2002
- TI Secondary nonaqueous electrolyte battery
- IN Aoki, Takashi
- PA GS-Melcotec Co., Ltd., Japan

PATENT NO. KIND DATE APPLICATION NO. DATE
PI JP 2002175807 A2 20020621 JP 2000-373846 20001208

PRAI JP 2000-373846 20001208

AB The battery uses an anode active mass mixture containing a carbonaceous material with a graphitized carbonaceous coating and having d. 1.3-1.6 g/cm3. Preferably, the carbonaceous material has d002 ≥0.330 nm, and the coated material has I1360/I1580 ≤0.3 (I1360 and I1580 are the intensities of peaks at 1360 and 1580/cm on the Ar laser Raman spectrum of the coated material).

IT 7782-42-5, Graphite, uses

RL: MOA (Modifier or additive use); USES (Uses)
 (carbonaceous material with graphitized coatings and
 controlled crystalline structure and d. for secondary
 lithium battery anodes)

RN 7782-42-5 HCAPLUS

CN Graphite (8CI, 9CI) (CA INDEX NAME)

С

- L83 ANSWER 4 OF 7 HCAPLUS COPYRIGHT ACS on STN
- AN 2002:104932 HCAPLUS Full-text
- DN 136:170203
- ED Entered STN: 08 Feb 2002
- TI Secondary lithium battery
- IN Okijima, Satoshi
- PA Denso Co., Ltd., Japan

	201120 001, -011,	<u>F</u>			
	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	JP 2002042887	A2	20020208	JP 2000-220605	20000721
_	0000 000605		00000701		

PRAI JP 2000-220605 20000721

- The battery uses LixNi1-yMyO2 (M = Co, Mn, Al, B, Ti, Mg, and/or Fe; $0 < x \le 1.2$, $0 \le y \le 0.25$) for cathode active mass, a carbonaceous material having a disordered layered structure on a crystalline graphite core for anode active mass; where the anode active mass has d 002 ≤ 0.340 nm and I1360/I1580 = 0.30-0.55 (I1360 and I1580 are the intensities of peaks at 1360 and 1580/cm on its Ar laser Raman spectrum).
- IT 7782-42-5, Graphite, uses

(anode active mass containing carbonaceous material on **graphite** cores for **secondary** lithium **batteries**)

- RN 7782-42-5 HCAPLUS
- CN Graphite (8CI, 9CI) (CA INDEX NAME)

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ΡI

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L83 ANSWER 6 OF 7 HCAPLUS COPYRIGHT ACS on STN
AN
    2001:134015 HCAPLUS Full-text
DN
    134:181079
    Entered STN: 23 Feb 2001
ΕD
    Nonaqueous electrolyte solutions and
TΙ
    secondary lithium batteries using the
    solutions
    Hamamoto, Shunichi; Abe, Hiroshi; Takai, Tsutomu; Ohira, Noriyuki; Ito,
IN
    Akikazu
    Ube Industries, Ltd., Japan
    PATENT NO. KIND DATE
                                        APPLICATION NO.
                                                               DATE
                                                                _____
                       ____
                              _____
                                          ______
     _____
    JP 2001052738
                        A2
                              20010223
                                         JP 2000-156622
                                                               20000526
PT
                       A
                              19990601
PRAI JP 1999-153334
     The electrolyte solns. contain cyclic carbonate, linear carbonate, and cyclic sultone derivs.
     having hydroxyalkanesulfonic acid content 1-1000 ppm. Secondary Li batteries use the electrolyte
     solns, and anodes composed of graphite having interplanar spacing d002 ≤0.34 nm.
    96-49-1, Ethylene carbonate 108-32-7, Propylene
TT
    carbonate
       (electrolyte solns. containing low
       hydroxyalkanesulfonic acid content cyclic sultone derivs. for
       secondary lithium batteries)
    96-49-1 HCAPLUS
RN
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CN

RN 108-32-7 HCAPLUS 1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME) CN

1,3-Dioxolan-2-one (9CI) (CA INDEX NAME)

7782-42-5, Graphite, uses IT (graphite with controlled interplanar spacing for anodes in secondary lithium batteries containing cyclic sultone derivs.)

```
L95 ANSWER 2 OF 30 HCAPLUS COPYRIGHT ACS on STN
    2003:884468 HCAPLUS Full-text
AN
    139:366951
DN
    Entered STN: 12 Nov 2003
ED
    Method for producing graphite aggregate for hydrogen absorption
TI
    Shirahiqe, Minoru; Iida, Junichi; Ito, Hitoshi; Katamura, Junji; Kawai,
IN
    Hitachi Funmatsu Yakin Co., Ltd., Japan; Nissan Motor Co., Ltd.
                   KIND DATE APPLICATION NO. DATE
    PATENT NO.
                       ----
                                         _____
                                                               _____
     -----
                   A2
                             20031111
                                         JP 2002-126296
                                                               20020426
    JP 2003321215
PT
                              20020426
PRAI JP 2002-126296
     The graphite aggregate comprising 1-40 nm of graphite crystal has an
     average particle size of 1-60 µm, a sp. surface area of ≥300 m2/g, an average pore diameter of
     \leq5.5 nm, an interlayer distance of 0.3360-0.3385 nm, and \geq0.3 cm3/g of pore volume of \leq5.0 nm of
     a pore radius. The aggregate contains ≥1 of Pt, Pd, Ni, K, Li, Ti, V, Cr, Mn, Fe, Co, Zr, and
     Nb. The product is light and reusable, and efficiently absorbs large amount of H2.
IT
     7439-93-2, Lithium, uses 7782-42-5, Graphite,
     RL: NUU (Other use, unclassified); USES (Uses)
        (method for producing graphite material for hydrogen
       absorption)
     7439-93-2 HCAPLUS
RN
     Lithium (7CI, 8CI, 9CI) (CA INDEX NAME)
CN
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Li

RN 7782-42-5 HCAPLUS CN Graphite (8CI, 9CI) (CA INDEX NAME)

С

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L95 ANSWER 3 OF 30 HCAPLUS COPYRIGHT ACS on STN
    2003:853394 HCAPLUS Full-text
AN
    139:326113
DN
    Entered STN: 31 Oct 2003
ED
    Powdery graphite-type anode material, anode, and
ΤI
     secondary lithium battery
     Fuse, Akira; Sato, Shuji; Nishioka, Keiko; Ishihara, Masashi
TN
    Mitsubishi Chemical Corp., Japan
PA
SO
     Jpn. Kokai Tokkyo Koho, 9 pp.
     CODEN: JKXXAF
DΨ
     Patent
     Japanese
LA
     ICM H01M004-58
IC
     ICS H01M004-02; H01M010-40; C01B031-04
     52-2 (Electrochemical, Radiational, and Thermal Energy Technology)
FAN.CNT 1
                                           APPLICATION NO.
                        KIND
                               DATE
     PATENT NO.
                                           _____
                        ____
     _____
     JP 2003308838
                         A2
                               20031031
                                           JP 2002-113045
                                                                  20020416
                               20020416
PRAI JP 2002-113045
CLASS
                CLASS PATENT FAMILY CLASSIFICATION CODES
 PATENT NO.
 _____
                       H01M004-58
 JP 2003308838 ICM
                TCS
                       H01M004-02; H01M010-40;
                       C01B031-04
     The claimed anode material comprises 50-99.5 parts graphite-type carbonaceous materials (G1) and
AB
     0.5-50 parts carbonaceous materials (G2) having lower crystallinity than G1 as total 100 parts,
     where the material is characterized by (1) x-ray diffractometry (XRD) peak intensities of (101)
     surface of rhombohedral graphite layer (ABS stacking layer) and (101) surface of hexagonal
     graphite layer (AB stacking layer) ABC(101)/AB(101) ≥0.01, (2) interplanar spacings
     (d002) of G1 <3.37 Å and (d002) of G2 \ge3.37 Å, and (3) initial charging-discharging efficiency at
     0-1.5 V cutoff potential using a Li counter electrode ≥70%. The claimed anode is obtained from a
     mixture containing the above material and a binder. The claimed battery is equipped with an
     electrolyte solution containing 10-99.5 weight% propylene carbonate or \gamma-butyrolactone and 0.1-10
     weight% film-forming agent, a cathode, and the above anode.
     7782-42-5, Graphite, uses
IT
     RL: DEV (Device component use); USES (Uses)
        (graphite powder containing carbonaceous coating for anode in
        lithium battery)
IT
     108-32-7, Propylene carbonate
     RL: DEV (Device component use); USES (Uses)
        (electrolyte solvent; graphite powder
        containing carbonaceous coating for anode in lithium battery)
     108-32-7 HCAPLUS
RN
     1,3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME)
CN
     872-36-6, Vinylene carbonate 4427-96-7
IT
     , Vinyl ethylene carbonate
        (film-forming agent, in electrolyte; graphite
        powder containing carbonaceous coating for anode in lithium battery)
     872-36-6 HCAPLUS
RN
     1,3-Dioxol-2-one (9CI) (CA INDEX NAME)
CN
     4427-96-7 HCAPLUS
RN
     1,3-Dioxolan-2-one, 4-ethenyl- (9CI) (CA INDEX NAME)
CN
     7782-42-5, Graphite, uses
IT
        (graphite powder containing carbonaceous coating for anode in lithium battery)
RN
     7782-42-5 HCAPLUS
CN
     Graphite (8CI, 9CI) (CA INDEX NAME)
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Entered STN: 14 Mar 2003
ED
     Graphite material for lithium ion secondary
TI
     battery negative electrode
     Yamazaki, Norimune; Kawamura, Toshifumi; Tamaki, Toshio
IN
     Kashima Oil Co., Ltd., Japan; Japan Energy Corp.; Nikko Materials Co.,
PΑ
     Ltd.; Petoca Materlias Ltd.
                       KIND
                                                                  DATE
                               DATE
                                           APPLICATION NO.
     PATENT NO.
                                                                   _____
                        ----
     _____
     JP 2003077473
                         A2
                                20030314
                                            JP 2001-270172
                                                                  20010906
PΙ
PRAI JP 2001-270172
                                20010906
     The graphite material has (A) a graphite interlayer distance (d002) ≤0.338 nm, a crystallite (Lc)
     .gtoreq.100 nm in the "c" axis direction, a crystallite (La) .gtoreq.100 nm in the "a" axis
     direction, and a diffraction peak ratio P101/P100≥2.0 as measured using x-ray diffraction method
     and (B) a Li metal counter electrode, and shows a flat area at 1.4 V(Li/Li+) in the discharge
     curve. The graphite material is obtained by graphitization of carbon fibers in the presence of a
     B compound The graphite material has an improved graphitization level, thereby increasing the
     charging and discharging capacities.
     graphite lithium ion secondary battery
ST
     neg electrode; graphitization boron compd
     7439-93-2, Lithium, uses
ΙT
     RL: DEV (Device component use); USES (Uses)
        (electrode; graphite material for lithium ion
        secondary battery neg. electrode)
     7439-93-2 HCAPLUS
RN
     Lithium (7CI, 8CI, 9CI) (CA INDEX NAME)
CN
 T.i
     7782-42-5, Graphite, uses
IT
     RL: DEV (Device component use); EPR (Engineering process); PEP (Physical,
     engineering or chemical process); PROC (Process); USES (Uses)
        (graphite material for lithium ion secondary
        battery neg. electrode)
     7782-42-5 HCAPLUS
RN
     Graphite (8CI, 9CI) (CA INDEX NAME)
CN
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L95 ANSWER 5 OF 30 HCAPLUS COPYRIGHT ACS on STN

2003:200683 HCAPLUS Full-text

AN

DN

С

138:240616

- L95 ANSWER 12 OF 30 HCAPLUS COPYRIGHT ACS on STN
- AN 2000:362767 HCAPLUS Full-text
- DN 133:7026
- ED Entered STN: 31 May 2000
- TI Carbon materials for anodes in **secondary nonaqueous- electrolyte batteries** and their manufacture by
 qraphitization
- IN Sakamoto, Hitoshi; Fujiura, Ryuji; Kanno, Koichi; Tosen, Takaaki; Sakai, Yukio; Takahashi, Yuzuru
- PA Mitsubishi Gas Chemical Co., Ltd., Japan

PATENT NO. KIND DATE APPLICATION NO. DATE

PI JP 2000149946 A2 20000530 JP 1998-322414 19981112

PRAI JP 1998-322414 19981112

- The C materials are nonscaly graphite powder having mosaic-type optical structure, c-axis direction crystallite size ≤ 100 nm, and an Raman band intensity ratio at 1360 and 1580 cm-1 (I1360/I1580) ≥0.1. The C materials are manufactured by heating granular or powdery mesophase pitch in a reactor at 400-800° under nonoxidizing atmospheric, grinding, and then graphitizing at ≥2000°. Batteries equipped with anodes using the C materials have high discharge capacity and charging efficiency.
- TT 7782-42-5P, Graphite, uses
 RL: DEV (Device component use); IMF (Industrial manufacture); PRP
 (Properties); PREP (Preparation); USES (Uses)
 (anodes containing specified graphite manufactured from mesophase
 pitch for secondary nonaq. batteries)
- RN 7782-42-5 HCAPLUS
- CN Graphite (8CI, 9CI) (CA INDEX NAME)

С

- L95 ANSWER 13 OF 30 HCAPLUS COPYRIGHT ACS on STN
- AN 2000:34367 HCAPLUS Full-text
- DN 132:80940
- ED Entered STN: 14 Jan 2000
- TI Graphite material for secondary lithium
 - battery and its manufacture
- IN Tamaki, Toshio; Hosotsubo, Tomimori
- PA Petoca, Ltd., Japan

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2000012034	A2	20000114	JP 1998-185710	19980617

PRAI JP 1998-185710 19980617

- The graphite material obtained by graphitization of carbon material at ≥2500° in the presence of B compds. show (a) the interlayer distance of the graphite layer (d002) ≤0.338 nm, (b) the size of C axis-oriented crystallite (Lc) ≥35 nm, (c) the size of a axis-oriented crystallite (La) ≥50 nm, (d) the peak intensity ratio of (101) and (100) diffraction peaks (P101/P100) ≥1.0, (e) the peak intensity ratio of raman spectroscopy at 1340 and 1580 cm-1 (I1340/I1580) ≥0.5, and (f) the existence of a shoulder-like peak (1310-1320 cm-1) with a peak at 1340 cm-1. In manufacture of the graphite material, the carbon material is kept at a constant temperature in 2200-2400° for ≥20 min. The material gives secondary lithium batteries with high initial charge-discharge efficiency.
- IT 7782-42-5P, Graphite, uses
 - RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
 - (fiber; manufacture of graphite material for secondary
 - lithium battery by graphitization of carbon material)
- RN 7782-42-5 HCAPLUS

С

CN Graphite (8CI, 9CI) (CA INDEX NAME)

```
1997:648805 HCAPLUS Full-text
AN
    127:320957
DN
   Entered STN: 11 Oct 1997
ED
   Lithium secondary batteries showing excellent cycling life
TI
    Maeda, Takeshi; Kurokawa, Hiroshi; Fujimoto, Masahisa; Noma, Toshiyuki;
IN
    Nishio, Koji
     Sanyo Electric Co., Ltd., Japan
PA
    PATENT NO. KIND DATE APPLICATION NO. DATE
                              -----
                                           -----
     _____
                        ____
                                         JP 1996-96195
     JP 09259884 A2
                               19971003
                                                                  19960325
PI
JP 3072049 B2
PRAI JP 1996-96195
                               20000731
                               19960325
     The title batteries comprise LiCo1-pNipO2 (p = 0.5-0.9) cathodes and Li-absorbing anodes
AΒ
     containing 3-8:2 mixts. of natural graphite having crystallite size Lc .gtoreq.1000 Å and d002
     spacing 3.35-3.36 \mathring{\mathbf{A}} and coke having Lc 10-150 \mathring{\mathbf{A}} and d002 3.40-3.70 \mathring{\mathbf{A}}.
     7782-42-5, Graphite, uses
IT
        (anode component; Li secondary batteries using Li
        Co Ni oxide cathodes)
     7782-42-5 HCAPLUS
RN
     Graphite (8CI, 9CI) (CA INDEX NAME)
CN
 C
IT
     7439-93-2, Lithium, uses
        (batteries; Li secondary batteries using
        Li Co Ni oxide cathodes)
     7439-93-2 HCAPLUS
RN
     Lithium (7CI, 8CI, 9CI) (CA INDEX NAME)
CN
```

L95 ANSWER 17 OF 30 HCAPLUS COPYRIGHT ACS on STN

Li

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ANSWER 18 OF 30 HCAPLUS COPYRIGHT ACS on STN
L95
    1997:552547 HCAPLUS Full-text
AN
DN
    127:151019
    Entered STN: 30 Aug 1997
ED
    Carbonaceous anode and compatible electrolyte for batteries
TI
    Barker, Jeremy; Gao, Feng
IN
PΑ
    Valence Technology, Inc., USA
                      KIND
                             DATE
                                         APPLICATION NO.
                                                              DATE
    PATENT NO.
                                                              _____
                                         ______
     _____
                       _---
                             _____
                             19970701
                                         US 1996-630402
                                                              19960410
                       A
ΡI
    US 5643695
    US 5660948
                       A
                             19970826
                                        US 1995-533882
                                                              19950926
    US 5759715
                       A
                             19980602
                                         US 1996-723195
                                                              19960927
                             19980127
                                         US 1996-740765
                                                              19961101
    US 5712059
                       A
                                        WO 1997-US3636
                                                             19970304
                       A1
                             19971016
    WO 9738459
                           19971029
                                                              19970304
                                       AU 1997-20733
    AU 9720733
                       A1
                                        US 1999-227342
                                                             19990108
                             20010227
                       E
    US 37076
                             19950926
PRAI US 1995-533882
                       A2
                       A2
                             19960410
    US 1996-630402
                       W
                             19970304
    WO 1997-US3636
```

The anode comprises graphite particles having an interlayer distance spacing of 002 planes as AB determined by x-ray diffraction of 0.330-0.340 nm, a crystallite size in the direction of c-axis of .gtorsim.90-.ltorsim.1000 nm, and ≥90 weight% of the graphite particles have a size of .ltorsim.24 μm . The electrolyte comprises a solvent mixture and a solute, the solvent mixture comprises ethylene carbonate (EC) and propylene carbonate (PC) and/or butylene carbonate (BC), with EC being present in an amount by weight which is at least as great as the amount of any other solvent. Optionally, the solvent mixture further comprises ≥1 organic solvent selected from Me Et carbonate, di-Et carbonate, di-Pr carbonate, and di-Me carbonate.

96-49-1, Ethylene carbonate IT

RL: TEM (Technical or engineered material use); USES (Uses) (battery electrolyte solvent mixture containing)

RN 96-49-1 HCAPLUS

1,3-Dioxolan-2-one (9CI) (CA INDEX NAME) CN

108-32-7, Propylene carbonate 4437-85-8, Butylene IT

RL: TEM (Technical or engineered material use); USES (Uses) (battery electrolyte solvent mixture containing ethylene carbonate and)

108-32-7 HCAPLUS RN

1.3-Dioxolan-2-one, 4-methyl- (9CI) (CA INDEX NAME) CN

4437-85-8 HCAPLUS RN

1,3-Dioxolan-2-one, 4-ethyl- (9CI) (CA INDEX NAME) CN

7782-42-5, Graphite, uses IT

RL: DEV (Device component use); USES (Uses)

(particles for battery anode)

7782-42-5 HCAPLUS RN

С

Graphite (8CI, 9CI) (CA INDEX NAME) CN

L95 ANSWER 19 OF 30 HCAPLUS COPYRIGHT ACS on STN

- AN 1997:341896 HCAPLUS Full-text
- 126:319385 DN
- Entered STN: 30 May 1997 ΕD
- ΤI Nonaqueous electrolyte lithium ion secondary

batteries

IN Barker, Jeremy

PA	Valence Technology PATENT NO.	Inc., KIND	USA DATE	APPLICATION NO.	DATE
PI	WO 9712409	A1	19970403	WO 1996-US13421	19960815
	US 5660948	A	19970826	US 1995-533882	19950926
	AU 9669546	A1	19970417	AU 1996-69546	19960815
	US 37076	E	20010227	US 1999-227342	19990108
PRAI	US 1995-533882	A	19950926		
	WO 1996-US13421	W	19960815		

Nonaq. electrochem. cells with improved performance can be fabricated by employing anodes AB comprising a composition having graphite particles that have a BET method sp. surface area of about 6 to about 12 m2/g and a crystallite height Lc of about 100 nm to about 120 nm, and wherein at least 90% (wt) of the graphite particles are less than 16 μm in size; a cathode; and a nonaq . electrolyte containing a solvent and salt that is interposed between the anode and cathode. When employed in an electrochem. cell, the anode can attain a specific electrode capacity of at least 300 mA-h/g. The electrochem. cell has a cycle life of greater than 1500 cycles, and has a first cycle capacity loss of only about 10% to about 15%.

12057-17-9, Lithium manganese oxide limn2o4 52627-24-4, TT

Cobalt lithium oxide

(cathodes; nonaq. electrolyte lithium ion secondary batteries)

ΙT 7782-42-5, Graphite, uses

(particles, anodes; nonaq. electrolyte lithium ion secondary batteries)

7782-42-5 HCAPLUS RN

С

Graphite (8CI, 9CI) (CA INDEX NAME) CN

```
Entered STN: 13 Jul 1996
ED
    Lithium ion secondary battery and manufacture of anode
TΙ
    active material for use in this battery
    Yamada, Kazuo; Mitate, Takehito; Yoneda, Tetsuya; Nishimura, Naoto
IN
    Sharp Kabushiki Kaisha, Japan
PΑ
    Eur. Pat. Appl., 21 pp.
SO
    CODEN: EPXXDW
DΤ
    Patent
    English
LA
    ICM H01M004-36
IC
    ICS H01M004-02; H01M010-40
    52-2 (Electrochemical, Radiational, and Thermal Energy Technology)
CC
FAN.CNT 1
                                                              DATE
    PATENT NO.
                      KIND
                             DATE
                                         APPLICATION NO.
                       ____
                             _____
                             19960522 EP 1995-303863
                                                             19950606
    EP 713256
                       A1
                       B1
                             20011212
    EP 713256
       R: DE, FR, GB
                                                              19941027
                   A2 19960517
                                         JP 1994-264005
    JP 08124559
                      B2
                             20011022
    JP 3222022
                                                             19950606
                                         US 1995-469926
    US 5576121
                       A
                             19961119
PRAI JP 1994-264005
                      · A
                             19941027
CLASS
              CLASS PATENT FAMILY CLASSIFICATION CODES
 PATENT NO.
 ______
               ICM H01M004-36
EP 713256
                     H01M004-02; H01M010-40
               ICS
     The anode of a Li ion secondary battery having a nonaq. ion conductor includes a primary active
AB
     material of a graphite which is capable of intercalation and deintercalation of Li ions and a
     secondary active material of CuO having a low crystallinity. The CuO has an x-ray diffraction
     pattern in which a peak representing (111) plane appears around 38.9° and its half-band width is
     ≥0.30°. The graphite has a spacing of (002) planes 0.335-0.340 nm, the crystallite size in the
     (002) plane direction ≥10 nm, and the crystallite size in the (110) plane direction ≥10 nm.
     graphite is coated with an amorphous C and the graphite: CuO weight ratio is 99:1 to 60:40.
     7439-93-2, Lithium, uses
IT
     RL: DEV (Device component use); USES (Uses)
       (battery anode from copper oxide and graphite intercalatable
       with)
    7439-93-2 HCAPLUS
RN
    Lithium (7CI, 8CI, 9CI) (CA INDEX NAME)
```

IT 7782-42-5, Graphite, uses

RL: DEV (Device component use); PRP (Properties); USES (Uses) (battery anode from copper oxide and lithium-intercalatable)

RN 7782-42-5 HCAPLUS

С

CN Graphite (8CI, 9CI) . (CA INDEX NAME)

L95 ANSWER 21 OF 30 HCAPLUS COPYRIGHT ACS on STN

1996:404751 HCAPLUS Full-text

AN DN

125:63151

Jeff Harrison, 22511, JEF-4B68

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L95 ANSWER 27 OF 30 HCAPLUS COPYRIGHT ACS on STN
```

AN 1990:122260 HCAPLUS Full-text

DN 112:122260

ED Entered STN: 31 Mar 1990

TI Graphite battery electrode and its manufacture

IN Suzuki, Tomonari; Wada, Hiroshi; Yoshimoto, Yoshikazu; Yoshida, Masaru; Nakajima, Shiqeo

PA Sharp Corp., Japan

PA	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
					-
ΡI	EP 346088	A1	19891213	EP 1989-305731	19890607
	EP 346088	B1	19971112		
	US 4978600	Α	19901218	US 1989-362505	19890607
	EP 717456	A2	19960619	EP 1995-202529	19890607
	EP 717456	A3	19961016		
	EP 1014462	A2	20000628	EP 2000-200483	19890607
	EP 1014462	A3	20020626		
	US 5080930	A	19920114	US 1990-580608	19900911
PRAI	JP 1988-141374	Α	19880608		
	EP 1989-305731	A3	19890607		
	EP 1995-202529	A3	19890607		
	US 1989-362505	A3	19890607		
	JP 1996-79958	A3	19960402		

The electrode graphite contains a high-crystalline graphite having interlayer spacing of 0.3354-0.3400 nm and a low- crystalline graphite having interlayer spacing of 0.343-0.355 nm. The ratio of the diffraction intensity at 2θ = 25.0° to the diffraction intensity of the peak corresponding to the (002) reflection at 2θ = 26.3° in the x-ray diffraction profile of the graphite is 0.03-0.90. The graphite is chemical vapor deposited at 450-1300° (700-1200°) from a hydrocarbon of mol. weight ≤150 on a substitute of Fe, Co, Ni, or an alloy of these metals. In charge-discharge test with Li counterelectrode in 1M LiClO4/propylene carbonate electrolyte, the invention graphite electrode.

IT 7439-93-2, Lithium, uses and miscellaneous

RL: USES (Uses)

(electrodes insertable with, graphite for, crystallinity of,

for batteries)

RN 7439-93-2 HCAPLUS

CN Lithium (7CI, 8CI, 9CI) (CA INDEX NAME)

Li

IT 7782-42-5, Graphite, uses and miscellaneous

RL: USES (Uses)

(electrodes, lithium-insertable, crystallinity of, for batteries)

RN 7782-42-5 HCAPLUS

CN Graphite (8CI, 9CI) (CA INDEX NAME)

С

L100 ANSWER 1 OF 3 HCAPLUS COPYRIGHT ACS on STN

AN 2000:707353 HCAPLUS Full-text

DN 133:282949

ED Entered STN: 06 Oct 2000

TI Carbon fiber, method for producing the same and electrode for cell

IN Nishimura, Kunio; Endo, Morinobu

A Showa Denko K. K., Japan

	a Denko K. K., NT NO.	Japan KIND	DATE	APPLICATION NO.	DATE
EP 1: US 64	000058536 191131 489026	A1 A1 B1	20001005 20020327 20021203 20030313	WO 2000-JP1835 EP 2000-911361 US 2001-937079 US 2002-268707	20000324 20000324 20010921 20021011
PRAI JP 19 US 19 JP 19 JP 20 WO 20	003049443 999-81260 999-145266P 999-307867 000-608813	A1 A P A A3 W	19990325 19990726 19991029 20000324 20000324	US 2002-268/07	20021011
US 20	001-937079	A3	20010921		

A fine and highly crystalline carbon fiber has a fiber diameter of $\leq 1~\mu m$, has a distance between layer faces d002 of 0.335-0.34 nm as measured by the X-ray diffraction method, satisfies the formula d002 <0.3448 - 0.0028(log Φ) wherein Φ is a diameter of a carbon fiber, and has an Lc (thickness along C axis of the crystal) of $\leq 40~nm$; where the fine carbon fiber contains boron in the crystal thereof. This fine carbon fiber can be produced by a method comprising providing a fine carbon fiber produced by the gas phase method, the arc discharge method, the laser method or the like as a raw material, adding boron or a boron compound to the raw material, compressing the resulting mixture so as for the mixture has a bulk d. of $\geq 0.05~g/cm3$ and subjecting the resultant product to a heat treatment at $\geq 2000^{\circ}$. A fine carbon fiber was prepared by the gas phase method, heated at 1200°, mixed with 120 g B4C, compressed in a mold, heated at 2900° for 60 min, and pulverized to give a fiber with length 5-30 μ m, d002 0.380 nm, and Lc value 29.0 nm.

L100 ANSWER 2 OF 3 HCAPLUS COPYRIGHT ACS on STN

AN 1998:545755 HCAPLUS Full-text

DN 129:191554

ED Entered STN: 27 Aug 1998

TI Graphite containing boron and nitrogen as anode material for lithium secondary battery and its manufacture

IN Suzuki, Kimihito; Hirano, Kaneji; Sasaki, Takeaki; Inada, Yukiteru; Sugiura, Tsutomu

PA Nippon Steel Corp., Japan; Nippon Steel Chemical Co., Ltd.

PATENT NO. KIND DATE APPLICATION NO. DATE

PI JP 10223223 A2 19980821 JP 1997-24038 19970206

PRAI JP 1997-24038 19970206

The anode material comprises graphite powders having spacing (d002) between C network layers in X-ray diffraction at wide diffraction angles d002 ≤0.337 nm and length of the crystal in the c axis direction Lc ≥40 nm and containing 0.1-10 atomic% B and 0.1-10 atomic% N. The anode material is manufactured by the following steps: (1) addition and mixing of 0.1-25 weight% (as. B) B compds. and 0.1-25 weight% (as. N) N compds. into C powders obtained from pitch and (2) heating of the resulting powders at ≥2500° for ≥0.1 h in an inert or reducing atmospheric The obtained powders contain highly graphitized crystals and the battery shows high discharge capacity and initial activity in cycling performance.

IT 7782-42-5P, Graphite, uses

RL: DEV (Device component use); PNU (Preparation, unclassified); PREP (Preparation); USES (Uses)

(graphite containing B and N as anode material for Li battery for capacity and cycling performance)

RN 7782-42-5 HCAPLUS

С

CN Graphite (8CI, 9CI) (CA INDEX NAME)

```
L103 ANSWER 1 OF 3 HCAPLUS COPYRIGHT ACS on STN
AN 2002:27695 HCAPLUS Full-text
    136:72324
DN
   Entered STN: 11 Jan 2002
ED
TI Secondary lithium battery using carbon anode active
    mass with bilayer structure
    Chiang, Tong Ping; Uenae, Keiichirou; Honkawa, Kenichi; Kawai, Takanobu
IN
    Hitachi Maxell Ltd., Japan; Nippon Carbon Co., Ltd.
SO
    Jpn. Kokai Tokkyo Koho, 8 pp.
    CODEN: JKXXAF
ÐΤ
    Patent
T.A
    Japanese
IC
    ICM H01M004-58
     ICS H01M004-02; H01M010-40
    52-2 (Electrochemical, Radiational, and Thermal Energy Technology)
FAN.CNT 1
                                          APPLICATION NO.
                       KIND DATE
    PATENT NO.
                        ----
                                                                  _____
     ______
                                                                20000623
PΤ
    JP 2002008656
                         A2
                               20020111 JP 2000-188762
PRAI JP 2000-188762
                               20000623
     The battery uses the active mass obtained by coating C particles having 002 lattice spacing
AB
     (d002) \le 0.350 \text{ nm}, crystallite size in c-axis direction (Lc) \ge 70 \text{ nm}, and aspect ratio (a/b) \ge 3
     with mesophase pitch and firing the coated particles so that the core particles have d002 \le 0.3365
     nm and Lc ≥100 nm. The battery has high capacity and charge-discharge cycle performance.
    7782-42-5, Graphite, uses
IT
```

(core C particle from; Li battery using C anode active mass with bilayer structure for high capacity and cycle performance)

RN 7782-42-5 HCAPLUS

Graphite (8CI, 9CI) (CA INDEX NAME) CN

```
AN 2000:905714 HCAPLUS Full-text
    134:44568
DN
   Entered STN: 27 Dec 2000
ED
    Graphite particles for secondary lithium
TΤ
    battery anodes, secondary lithium battery
    anodes, and secondary lithium batteries
    Takei, Koichi
IN
    Hitachi Chemical Co., Ltd., Japan
                                     APPLICATION NO. DATE
    PATENT NO. KIND DATE
    _____
                     ----
                                      _____
PI JP 2000357512
                            20001226 JP 1999-166142 19990614
                     A2
                            19990614
PRAI JP 1999-166142
CLASS
            CLASS PATENT FAMILY CLASSIFICATION CODES
PATENT NO.
 _____
                    -----
JP 2000357512 ICM H01M004-58
               ICS H01M004-02; H01M010-40
    The dispersions of the graphite particles have pH 5.2-6.1 when dispersed in 25 weight equivalent
AB
    pure water. The graphite particles may have interplanar spacing (d002) ≤0.337 nm and c axis
    crystallite length (Lc) ≥50 nm. Secondary lithium battery anodes containing the above stated
    graphite particles and secondary lithium batteries comprising of the anodes and Li compound-
     containing cathodes are also claimed. Safe batteries with large discharge capacity are
    manufactured
IT
    7782-42-5P, Graphite, uses
       (graphite particles with certain pH for anodes in
       secondary lithium batteries for large discharge
       capacity)
    7782-42-5 HCAPLUS
RN
```

С

Graphite (8CI, 9CI) (CA INDEX NAME) CN

L103 ANSWER 2 OF 3 HCAPLUS COPYRIGHT ACS on STN

```
L106 ANSWER 2 OF 9 HCAPLUS COPYRIGHT ACS on STN
    2001:710102 HCAPLUS Full-text
DN
    135:259802
    Entered STN: 28 Sep 2001
ED
    Secondary battery using lithium-intercalatable carbon
ΤI
    anode and its manufacture
    Tsushima, Manabu; Morimoto, Takeshi; Kuruma, Isamu
IN
    Asahi Glass Co., Ltd., Japan
PA
                                                            DATE
                                      APPLICATION NO.
    PATENT NO.
                    KIND DATE
                                       -----
                      ____
                             -----
    _____
                                        JP 2000-72717 20000315
    JP 2001266872
                     A2
                             20010928
ΡI
PRAI JP 2000-72717
                             20000315
CLASS
            CLASS PATENT FAMILY CLASSIFICATION CODES
 PATENT NO.
               ----
 JP 2001266872 ICM
                     H01M004-58
               ICS H01M010-40
     The battery has an activated C cathode, a Li-intercalatable C anode, and a Li salt-containing
ΑB
     organic electrolyte, where the Li-intercalatable C is a graphite having interplanar spacing in
     [002] plane (d002) 0.335-0.336 nm, crystallite size (Lc) 10-100 nm, and crystallite size (La) 10-
     100 nm which are measured by x-ray diffraction. The graphite is manufactured by the following
     steps: (1) reacting concentrated H2SO4 with a graphite having d002 0.335-0.336 nm, Lc >200 nm,
     and La >200 nm, (2) washing with water, (3) drying, and (4) rapidly heating at 200-800^{\circ}. The
     battery has high withstand voltage and large capacity and shows excellent high-rate cycling
     performance.
```

IT **7782-42-5, Graphite,** uses

RL: DEV (Device component use); PEP (Physical, engineering or chemical process); PRP (Properties); PROC (Process); USES (Uses) (reacting graphite with concentrated H2SO4 for manufacturing anode active mass with controlled crystal structure for battery with high withstand voltage)

RN 7782-42-5 HCAPLUS

С

CN Graphite (8CI, 9CI) (CA INDEX NAME)

```
L106 ANSWER 3 OF 9 HCAPLUS COPYRIGHT ACS on STN
    2000:484271 HCAPLUS Full-text
AN
    133:92006
DN
    Entered STN: 18 Jul 2000
ED
TI
    Graphite fibers, manufacture of graphite fibers, and
    secondary lithium batteries
IN
    Abe, Hiroshi; Murai, Kenji
    Nikkiso Co., Ltd., Japan
PA
SO
    Jpn. Kokai Tokkyo Koho, 11 pp.
    CODEN: JKXXAF
DΤ
    Patent
    Japanese
LA
    ICM D01F009-127
TC
     ICS H01M004-58; H01M010-40
     52-2 (Electrochemical, Radiational, and Thermal Energy Technology)
     Section cross-reference(s): 57
FAN.CNT 1
                                         APPLICATION NO.
                                                              DATE
    PATENT NO.
                       KIND
                              DATE
     _____
                       ----
    JP 2000199131
                        A2
                              20000718
                                          JP 1998-374511
                                                              19981228
PRAI JP 1998-374511
                              19981228
CLASS
              CLASS PATENT FAMILY CLASSIFICATION CODES
 PATENT NO.
 ______
 JP 2000199131 ICM D01F009-127
               ICS H01M004-58; H01M010-40
     Graphite materials having (002) plane spacing ( d002) 0.3354-0.3362 nm and crystallite size in c
AB
     axis ≥70 nm are impact-treated to give graphite fibers having average grain diameter (d50%;
     determined by laser scattering) 8-15 \mu m. The fibers and secondary lithium batteries with anodes
     comprising the graphite fibers, Li mixed oxide cathodes, and Li- and organic solvent-containing
     electrolytes are also claimed. Batteries with excellent cycle characteristics, high discharge
     capacity, and excellent charge-discharge characteristics are obtained.
     7782-42-5, Graphite, uses
     RL: DEV (Device component use); PEP (Physical, engineering or chemical
     process); TEM (Technical or engineered material use); PROC (Process); USES
        (fibers; manufacture of graphite fibers with controlled crystalline
       properties and their use in secondary lithium
       batteries)
     7782-42-5 HCAPLUS
RN
    Graphite (8CI, 9CI) (CA INDEX NAME)
CN
 С
TТ
     7440-44-0, Carbon, processes
     RL: PEP (Physical, engineering or chemical process); PROC (Process)
        (whiskers; manufacture of graphite fibers with controlled
       crystalline properties and their use in secondary lithium
       batteries)
     7440-44-0 HCAPLUS
RN
     Carbon (7CI, 8CI, 9CI) (CA INDEX NAME)
CN
```

С

L106 ANSWER 5 OF 9 HCAPLUS COPYRIGHT ACS on STN 1998:184496 HCAPLUS Full-text AN 128:259554 DN ED Entered STN: 28 Mar 1998 TI Carbon anodes for nonaqueous electrolyte batteries and Takanishi, Keijirou; Adachi, Masaya; Nakae, Takeji; Matsuda, Yoshio; Inoue, Takeharu PA Toray Industries, Inc., Japan Jpn. Kokai Tokkyo Koho, 10 pp. SO PATENT NO. KIND DATE APPLICATION NO. DATE ____ _____ _____ -----PI JP 10079252 PRAI JP 1996-234089 19980324 JP 1996-234089 19960904 A2 19960904 CLASS PATENT NO. CLASS PATENT FAMILY CLASSIFICATION CODES _____ JP 10079252 ICM H01M004-58 ICS H01M004-02; H01M010-40 The title anodes comprise (A) amorphous C having a laminated layer structure, C content (Ps, as AB weight) ≥ 0.54 and < 0.85, thickness of c-axis crystallite (Lc) 1.0-2.0 nm, and N/C atomic ratio 0.005-0.055, and (B) crystalline C powders having interplanar spacing d002 ≤0.34 nm and Lc 20-100 nm. Preferably, the amorphous C has d002 0.345-0.365 nm. The anodes show high discharge capacity and and excellent cycling property. 7782-42-5, Graphite, uses TΤ RL: DEV (Device component use); USES (Uses)

(nonaq. electrolyte secondary

batteries using C anodes containing layered amorphous C and crystalline graphite)

7782-42-5 HCAPLUS RN

С

Graphite (8CI, 9CI) (CA INDEX NAME) CN

L106 ANSWER 6 OF 9 HCAPLUS COPYRIGHT ACS on STN

AN 1997:334835 HCAPLUS Full-text

DN 126:307275

ED Entered STN: 26 May 1997

TI Process for production of graphitic electrode material for nonaqueous secondary battery

IN Sonobe, Naohiro; Masuko, Jiro; Hoshi, Akio

PA Kureha Kagaku Kogyo Kabushiki Kaisha, Japan

]	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI I	EP 766328	A1	19970402	EP 1996-306980	19960925
,	JP 09092284	A2	19970404	JP 1995-273440	19950926
τ	JS 5721071	A	19980224	US 1996-718939	19960924
(CA 2186442	AA	19970327	CA 1996-2186442	19960925
PRAI	JP 1995-273440		19950926		

CLASS

PATENT NO. CLASS PATENT FAMILY CLASSIFICATION CODES

EP 766328 ICM **H01M004-58**

A graphitic electrode material suitable for use in a nonaq. solvent-type secondary battery is provided. The graphitic material is characterized by an average (002)-plane spacing d002 of 0.336-0.345 nm, a crystallite size along c-axis Lc(002) of 15-60 nm, and a lattice strain & of at most 2.0 + 10-2 nm-1 as measured by X-ray diffraction method. The graphitic material may suitably be formed through a process including the steps of: thermally polymerizing a condensed polycyclic aromatic compound in the presence of a Lewis acid catalyst to form a polymerizate, and heat-treating the polymerizate at 2100-2600° under a reduced pressure or in an inert gas atmospheric The graphite electrode material exhibits large doping and dedoping capacities which provide only a small difference there-between (i.e., irreversible capacity) and cause only a small decrease at the time of quick charging and discharging.

L106 ANSWER 9 OF 9 HCAPLUS COPYRIGHT ACS on STN AN 1994:275403 HCAPLUS Full-text DN 120:275403 ED Entered STN: 28 May 1994 TI Secondary nonaqueous lithium batteries IN Suzuki, Kimihito; Iijima, Takashi; Sato, Maki PA Nippon Steel Corp, Japan; Shinnittetsu Kagaku PATENT NO. KIND DATE APPLICATION NO. DATE -------------------JP 05325968 A2 I JP 1992-157384 -----JP 1992-157384 19931210 19920526 PΙ 19920526 PRAI JP 1992-157384 CLASS

CLASS PATENT FAMILY CLASSIFICATION CODES PATENT NO. ______ ---**---**____ ICM H01M004-58 JP 05325968 ICS H01M010-40

The batteries use LiCoxNi1-xO2 (x = 0-1) as cathode active masses and pitch-based carbon fibers AΒ or their powders having C layer lattice spacing (d002) ≤0.343 nm and c-axis crystallite size (Lc) ≥10 nm as anode active masses. The batteries have high cycle performance and are suitable for portable devices.

- L107 ANSWER 1 OF 12 HCAPLUS COPYRIGHT ACS on STN
- AN 2003:460421 HCAPLUS Full-text
- DN 139:23744
- ED Entered STN: 17 Jun 2003
- TI Manufacture of graphite by low temperature graphitization
- IN Hoshi, Kazuto; Ota, Naoto; Sogabe, Toshiaki
- PA Tovo Tanso Co., Japan

•••	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2003171109	A2	20030617	JP 2001-369638	20011204
PRAI	JP 2001-369638		20011204		

- AB Graphitization of carbonaceous raw materials is carried out by previously mechanochem. mixing graphitization catalysts selected from Mn, Mn alloys, and Mn compds. The obtained graphite has (002) plane spacing d002 ≤0.3375 nm, and crystallite size along with c-axis direction ≥10 nm. Since the graphitization proceeds at .apprx.1300° in the presence of the catalysts, the manufacturing process is of energy saving.
- IT 7782-42-5P, Graphite, preparation
 - RL: IMF (Industrial manufacture); PREP (Preparation) (manufacture of graphite by low temperature graphitization of carbonaceous materials mixed with manganese-containing catalysts)
- RN 7782-42-5 HCAPLUS
- CN Graphite (8CI, 9CI) (CA INDEX NAME)

- L107 ANSWER 2 OF 12 HCAPLUS COPYRIGHT ACS on STN
- AN 2001:617309 HCAPLUS Full-text
- DN · 135:183277
- ED Entered STN: 24 Aug 2001
- TI Secondary nonaqueous-electrolyte
 - battery with carbon anode
- IN Hashimoto, Tomotaka; Yamashita, Masataka; Ohashi, Masahiro; Kanekiyo, Hiroshi
- PA Asahi Chemical Industry Co., Ltd., Japan
- SO Jpn. Kokai Tokkyo Koho, 7 pp.

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2001229916	A2	20010824	JP 2000-38743	20000216

PRAI JP 2000-38743 20000216

- The battery is equipped with an anode having Li intercalation coefficient K ≥0.70. Preferably, the anode comprises a C material having interplanar spacing d002 ≥0.3350 nm and <0.3380 nm, the size of c axis-oriented crystallite (Lc) ≥10 nm, average crystal size 10-30 µm, and sp. surface area ≤5 m2/g. The C material may be covered with nongraphitic C. The battery has long cycle life at low temperature
- IT 7782-42-5, KS 44, uses
 - RL: DEV (Device component use); USES (Uses)
 - (secondary nonaq.-electrolyte
 - battery with specified carbon anode)
- RN 7782-42-5 HCAPLUS
- CN Graphite (8CI, 9CI) (CA INDEX NAME)

L107 ANSWER 5 OF 12 HCAPLUS COPYRIGHT ACS on STN

AN 1998:398674 HCAPLUS Full-text

DN 129:43358

ED Entered STN: 29 Jun 1998

TI Secondary lithium ion battery anode material and its

IN Tamaki, Toshio; Maeda, Takashi

PA Petoca, Ltd., Japan

PRAI JP 1996-331410 19961128

The anode material of BN-free **graphite** prepared by graphitizing with B compound under N atmospheric and reheating in vacuum or halogen gas atmospheric has x-ray diffraction measurement results as follows: **graphite layer distance** (d002) ≤0.338 nm, C-axis direction crystallite size (LC) ≥35 nm, a-axis direction crystallite size (La) ≥50 nm, and ratio of (101) diffraction peak to (100) diffraction peak (P101/P100) ≥1.0. The anode material is manufactured by using mesophase pitch as raw material, spinning, infusibilizing, optionally carbonizing at ≤1500°, milling, adding B compound to the milled article, graphitizing the article at ≥2200° in N, and reheating the resulting material at ≥2000° in vacuum or halogen gas atmospheric The material as milled **graphite** fiber improves discharge capacity of the battery.

L118 ANSWER 1 OF 13 WPIX COPYRIGHT THOMSON DERWENT on STN

AN 2004-244688 [23] WPIX Full-text

DNN N2004-194226

DNC C2004-095954

TI Negative electrode material for non-aqueous electrolyte secondary battery, comprises graphite particles having preset diameter, surface area, size and specific gravity, coated with carbon precursor.

PA (TOJW) TOKAI CARBON KK

PI JP 2004079344 A 20040311 (200423)*

13 H01M004-58

ADT JP 2004079344 A JP 2002-238055 20020819

PRAI JP 2002-238055

20020819

JP2004079344 A UPAB: 20040405

NOVELTY - Negative electrode (1) material comprises graphite particles coated with 2 layer structure of carbon material formed by heat-processing at 800-2800 deg. C. Particles have average particle diameter of 10-40 mu m, specific surface area of 10 m2/g or less, true specific gravity of 2.18-2.25 and tapping specific gravity of 1-1.3. Face distance of graphite surface (002) by X-ray diffraction is 100 nm or more.

DETAILED DESCRIPTION - The negative electrode material comprises graphite particles obtained by machine-grinding and classifying, as nucleus. The nucleus surface includes carbon precursor. The particles have 2 layer structure of carbon material formed by heat-processing at 800-2800 deg. C under inert atmosphere. The particles have average particle diameter of 10-40 mu m, specific surface area of 10 m2/g or less, true specific gravity of 2.18-2.25 and tapping specific gravity of 1-1.3. The face distance of the graphite microcrystal surface (002) by X-ray diffraction is 100 nm or more. The size of microcrystal in C axial direction is 0.337 nm or less. The ratio of peak intensity of particles at 1580 cm-1 and at 1360 cm-1 in argon ion laser Raman spectrum, is more than 0.5. The half-value width of particles at 1580 cm-1 is more than 26 cm-1.

USE - For non-aqueous electrolyte secondary battery such as lithium ion battery.

ADVANTAGE - The negative electrode material provides secondary battery with excellent initial stage charging and discharging efficiency, high reversible cell capacitance and durability.

DESCRIPTION OF DRAWING(S) - The figure shows sectional drawing of coin-type battery used in order to measure the capacitance maintenance factor of battery.

Negative electrode 1

Positive electrode 2

Separator 3

Negative pole can 4

Positive pole can 5

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2000-664931 [64]
                        WPIX Full-text
AN
                        DNC C2000-201394
DNN N2000-492816
     Fine and high crystalline carbon fiber for use as a
ΤI
     filler material for various batteries, ceramics, and resins, has a fiber
     diameter of 1 micron or less and an Lc of 40 nm or less, and it contains
     boron.
DC
     E36 F01 L03 P73 X16
IN
     ENDO, M; NISHIMURA, K
     (SHOW) SHOWA DENKO KK
PA
CYC
    93
                    A1 20001005 (200064)* JA
PΙ
     WO 2000058536
                                                       D01F009-127
                    A 20001016 (200106)
     AU 2000033282
                                                       D01F009-127
                    A1 20020327 (200229) EN
     EP 1191131
                                                       D01F009-127
     KR 2001110680 A 20011213 (200237)
                                                       H01M004-96
                    A 20020403 (200247)
                                                       D01F009-127
     CN 1343269
     JP 2000608813 X 20020709 (200259)
                                                       D01F009-127
     US 6489026 B1 20021203 (200301)
                                                       D01F009-12
     US 2003049443 A1 20030313 (200321)
                                                       D02G003-00
     TW 524904 A 20030321 (200365)
JP 3461805 B2 20031027 (200373)
                                                       D01F009-12
                                                13
                                                       D01F009-127
     JP 2004003097 A 20040108 (200405)
                                                       D01F009-127
                                                20
                                                       H01M004-96
     KR 428899
                    B 20040429 (200457)
                          19991029; JP 1999-81260
PRAI JP 1999-307867
     19990325; US 1999-145266P
                                    19990726
     WO 200058536 A UPAB: 20040205
AB
     NOVELTY - A fine and high crystalline carbon fiber having a fiber diameter of 1 mu or less and an
     Lc of 40 nm or less, is for use as a filler material for various batteries, ceramics, resins,
           DETAILED DESCRIPTION - The carbon fiber has a distance between layer faces d002 of 0.335 to
      0.342 nm as measured by the X-ray diffraction method and has dimensions that satisfy the
      following relationship.
             d002 less than 0.3444 - 0.0028 (log phi )
           Lc = length along the c axis;
           phi = diameter of a carbon fiber.
           USE - The carbon fiber is used as a filler for electrodes of batteries, for resins,
      ceramics, etc..
           ADVANTAGE - The carbon fiber contained in electrodes of batteries improves their electric
      and thermal conductivity. The carbon fiber imparts strength to ceramics, resins, metals, etc.
TECH WO 200058536 AlUPTX: 20001209
     TECHNOLOGY FOCUS - INORGANIC CHEMISTRY - Preferred fiber : The Raman
     spectrum of the fiber has an R-value of 0.5 and a half peak width at
     1580 cm-1 of 20 - 40 cm-1. The fiber diameter is 1 mum or less.
     The fiber contains 0.1 - 3 wt % of boron inside the crystal. The carbon
     fiber preferably has a fiber diameter of 0.01 - 1 micrometer and an aspect
     ratio of 10 or more. The powder resistance along the vertical direction
     when the fiber is pressurized into a density of 0.8 g/cm3 is 0.01 \mbox{Ohm} \times \mbox{cm}
     or less. The carbon fiber is produced in the gas phase.
     Preferred Process : The carbon fiber is produced by adding boron or a
     boron compound to fine carbon fiber having a diameter of 1 mum or less
     until the bulk density becomes 0.05 g/cm3 or more and heat-treating at
     2000 degreesC or higher. The amount of boron or boron compound is 0.1 - 10
     wt%. The electrode for batteries contains 0.1 - 20 wt% of the invented
     carbon fiber.
ABEX WO 200058536 AlUPTX: 20001209
     EXAMPLE - Carbon fibers made by thermal decomposition of benzene in the gas phase was heat-
      treated at 1200 degreesC. The obtained flock carbon fibers were crushed so as to have a bulk
      density of 0.02 \text{ g/cm}3 and a length of 10 - 10 \text{ mum}. B4C powder ( 120 \text{ g} ) was added to the obtained
      fiber and mixed using a Henshel mixer. The mixture was placed in a graphite crucible and
      compressed until the bulk density became 0.075 g/cm3. The mixture in the crucible was heated at
      2900 degreesC for 60 min, and crushed at RT. The obtained fine carbon fiber contained 1.03 wt% of
      boron and had a d002 value of 0.380 nm and an Lc of 29 nm.
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L118 ANSWER 2 OF 13 WPIX COPYRIGHT THOMSON DERWENT on STN

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L118 ANSWER 3 OF 13 WPIX COPYRIGHT THOMSON DERWENT on STN
AN
    2000-352721 [31] WPIX Full-text
DNN N2000-264329
                        DNC C2000-107570
     Carbon material for electrode of non aqueous secondary battery used
     specifically as anode in a secondary cell with quick discharging and
     charging property.
     ISHIHARA, T; KAMEDA, T
IN
     (MITU) MITSUBISHI CHEM CORP
PA
                                                        H01M004-58
     EP 1005097
                    A1 20000531 (200031) * EN
                                                 21
PΙ
     JP 2000223120
                    A 20000811 (200044)
                                                        H01M004-58
     CN 1261729 A 20000802 (200058)
JP 2000340232 A 20001208 (200104)
KR 2000035742 A 20000626 (200111)
                                                        H01M004-58
                                                        H01M004-58
                                                13
                                                        H01M004-58
     TW 459416 A 20011011 (200368)
                                                        H01M004-58
                                                        H01M010-24
     JP 3534391 B2 20040607 (200437)
                                                  13
                                                        H01M004-58
PRAI JP 1999-80904
                          19990325; JP 1998-336796 19981127
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AB EP 1005097 A UPAB: 20000630

NOVELTY - Carbonaceous material for electrode comprises a plane space d002 of a (002) plane less than 0.337 nm in an x-ray wide angle diffraction method, a crystallite size (c) of 90 nm or higher, an R value as a peak intensity ratio of a peak intensity of 1360 cm-1 to 1580 cm-1 in a Raman spectrum in use of an argon ion laser of 0.02 or higher, and a tap density of 0.75 g/cm3 or higher.

DETAILED DESCRIPTION - ADDITIONAL CLAIMS are included for:

- (a) a multilayer structure carbonaceous material for an electrode, produced by mixing the carbonaceous material with organic compound(s) and carbonizing the organic compound; and
- (b) a non aqueous solvent secondary battery comprising anode and non aqueous electrolyte of solute and non aqueous electrolyte.

USE - None given.

ADVANTAGE - Battery has adequate quick charging and discharging property.

- L118 ANSWER 4 OF 13 WPIX COPYRIGHT THOMSON DERWENT on STN
- AN 1997-213197 [19] WPIX Full-text
- CR 1997-350225 [32]; 1998-119966 [11]; 1998-332107 [29]
- DNN N1997-175812 DNC C1997-068911
- Non-aqueous lithium ion electrochemical cell with improved performance has cathode and non-aqueous electrolyte with solvent and salt with cathode and anode having composition of graphic particles with BET method surface area of about 6 to 12 m 2 per g, and crystalline height of about 100 nm to 120 nm.
- IN BARKER, J
- PA (VALE-N) VALENCE TECHNOLOGY INC
- PI WO 9712409 A1 19970403 (199719)* EN 37 H01M004-58 AU 9669546 A 19970417 (199732) H01M004-58 US 5660948 A 19970826 (199740) 14 H01M004-62 US 37076 E 20010227 (200114) H01M004-62
- PRAI US 1995-533882 19950926; US 1999-227342 19990108
- AB WO 9712409 A UPAB: 20010312

The electrochemical cell includes an anode with a composition having graphite particles that have a BET method specific surface area of about 6 to 12 m2 per g. The particles have a crystalline height of about 100 nm to about 120 nm, or higher, and at least 90 percent by weight of the graphite particles are less than 16 micrometre in size.

A cathode is also included, and a non-aqueous electrolyte containing a solvent and salt interposed between the anode and the cathode. The graphite particles have a median size of about 8.1 micrometre, and are anisotropic.

ADVANTAGE - Cell demonstrates superior performance and can be fabricated employing anodes comprising graphite of extra **high crystallinity** and purity.

Dwg.0/5

ABEO US 5660948 A UPAB: 19971006

An electrochemical cell comprising: an anode comprising a composition comprising a polymer binder and a lithium intercalation carbon material in the form of graphite particles that have a BET method specific surface area of about 6 to about 12 m2/g, a crystallite height 2.265 g/cm3, where at least 90% (wt) of the graphite particles are less than 16 mu m in size and where the polymer binder comprises about 80% (wt) or more of the composition; a cathode; and a non-aqueous electrolyte containing a solvent and salt that is interposed between the anode and cathode.

- L118 ANSWER 6 OF 13 JAPIO (C) JPO on STN
- AN 2003-100294 JAPIO Full-text
- TI NEGATIVE ELECTRODE ACTIVE MATERIAL FOR BATTERY AND NONAQUEOUS ELECTROLYTE
- BATTERY USING THE SAME
- IN INAMASU TOKUO; YOSHIDA HIROYUKI; ONDA TOSHIYUKI; NAKAGAWA HIROE
- PA YUASA CORP
- PI JP 2003100294 A 20030404 Heisei
- AI JP 2001-291637 (JP2001291637 Heisei) 20010925
- PRAI JP 2001-29163720010925
- SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 2003
- IC ICM H01M004-58
 - ICS C01B031-04; H01M004-02; H01M010-40
- PROBLEM TO BE SOLVED: To provide a negative electrode active material for a battery, of which the energy density is high, and the cycle characteristics and rate characteristics of charging/discharging and temperature performance are superior, and to provide a nonaqueous electrolyte battery using the negative electrode active material. SOLUTION: A carbonaceous material A consisting of a graphite containing the rhombic system structure at a composition ratio of more than 15% is coated with a carbonaceous material B containing no rhombic system structure to form a negative electrode active material for the nonaqueous electrolyte battery. It is desirable that Lc representing the size of crystallites is more than 100 nm in the carbonaceous material A, and that the specific surface are of the negative electrode active material measured by the BET (Brunauer-Emmett- Teller) method is 3 m<SP>2</SP>/g or less. It is also desirable that the nonaqueous electrolyte battery using the above negative electrode active material has such a nonaqueous electrolyte that is contains carbonate having double-bond structures, and further contains propylene carbonate. COPYRIGHT: (C) 2003, JPO

- L118 ANSWER 7 OF 13 JAPIO (C) JPO on STN
- AN 2001-266872 JAPIO Full-text
- TI SECONDARY POWER SOURCE AND ITS MANUFACTURING METHOD
- IN TSUSHIMA MANABU; MORIMOTO TAKESHI; KURUMA ISAMU
- PA ASAHI GLASS CO LTD
- PI JP 2001266872 A 20010928 Heisei
- AI JP 2000-72717 (JP2000072717 Heisei) 20000315
- PRAI JP 2000-7271720000315
- SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 2001
- IC ICM H01M004-58
 - ICS H01M010-40
- PROBLEM TO BE SOLVED: To provide a secondary power source that has a high voltage resistance, a high capacity and is excellent in rapid charge and discharge cycle characteristics. SOLUTION: The secondary power source comprises a positive electrode composed mainly of activated charcoal, a negative electrode composed mainly of a graphite which has a surface space of 0.335-0.336 nm at (002) face as measured by X-rays diffraction and a crystallite size of Lc of 10-100 nm, La of 10-100 nm and which stores and separates lithium ion, and an organic electrolyte containing lithium salt. COPYRIGHT: (C)2001, JPO

- L118 ANSWER 8 OF 13 JAPIO (C) JPO on STN
- AN 2000-340232 JAPIO Full-text
- TI CARBON MATERIAL FOR ELECTRODE AND NONAQUEOUS SECONDARY BATTERY USING THE SAME
- IN KAMEDA TAKASHI; ISHIHARA MASAJI
- PA MITSUBISHI CHEMICALS CORP
- PI JP 2000340232 A 20001208 Heisei
- AI JP 1999-327768 (JP11327768 Heisei) 19991118
- PRAI JP 1998-33679619981127
 - JP 1999-8090419990325
- SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 2000
- IC ICM H01M004-58
 - ICS C01B031-02; H01M010-40
- PROBLEM TO BE SOLVED: To provide a carbon material for an electrode having a high electrode filling property, high energy density, and an excellent quick charging/discharging property. SOLUTION: In this carbon material for an electrode, a surface interval (d002) by a wide angle X-ray diffraction method (002) is less than 0.337 nm, the crystallite size (Lc) is 90 nm or larger, R value which is the ratio of the peal intensity of 1360 cm-1 versus the peak intensity at 1580 cm-1 is 0.2 or more, and a tap density is 0.75 g/cm3 or more. COPYRIGHT: (C) 2000, JPO

L118 ANSWER 10 OF 13 EUROPATFULL COPYRIGHT WILA on STN

PATENT APPLICATION - PATENTANMELDUNG - DEMANDE DE BREVET

AN 1005097 EUROPATFULL ED 20000611 EW 200022 FS OS Full-text

TIEN Carbonaceous material for electrode and non-aqueous solvent secondary

battery using this material.

IN Kameda, Takashi, Mitsubishi Chemical Corporation, Tsukuba Research

PA MITSUBISHI CHEMICAL CORPORATION, 5-2 Marunouchi 2-chome, Chiyoda-ku,

PI EP 1005097 A1 20000531 PRAI JP 1998-336796 19981127

JP 1999-80904 19990325

A carbonaceous material has a plane space d002 of a (002) plane less than 0.337 nm in an X-ray wide angle diffraction method, a crystallite size (Lc) of 90 nm or higher, an R value, as a peak intensity ratio of a peak intensity of 1360 cm.sup-1. to a peak intensity of 1580 cm.sup-1. in a Raman spectrum in use of an argon ion laser, of 0.20 or higher, and a tap density of 0.75 g/cm.sup3. or higher. Also disclosed is a multilayer structure carbonaceous material for electrode, which is manufactured by carbonizing some organic compounds where the carbonaceous material for electrode is mixed with the organic compounds. The battery using the carbonaceous material for electrode or the multilayer structure carbonaceous material for electrode has a large capacity, a small irreversible capacity admitted in the initial cycle, excellent capacity maintaining rate of the cycle, and particularly, largely improved quick charging and discharging characteristics.

CLMEN 1. A carbonaceous material for electrode comprising a plane space d002 of a (002) plane less than 0.337 nm in an X-ray wide angle diffraction method, a crystallite size (Lc) of 90 nm or higher, an R value, as a peak intensity ratio of a peak intensity of 1360 cm.sup-1. to a peak intensity of 1580 cm.sup-1. in a Raman spectrum in use of an argon ion laser, of 0.20 or higher, and a tap density. . . 4. . . . carbonaceous material for electrode according to any of claim 1 to claim 3, wherein the carbonaceous material has an average particle size of 2 to 50 µm.

5. . . . any of claim 1 to claim 4, wherein the carbonaceous material has a half value width of a peak of 1580 cm.sup-1. in the Raman spectrum in use of the argon ion laser, of 20 cm.sup-1. or higher.

9. . . claim 7 or claim 8, wherein the carbonaceous material is graphitized powders or carbonaceous powders which have a plane space d002 of the (002) plane less than 0.340 nm in the X-ray wide angle diffraction method, a crystallite size (Lc) of 30 nm or higher, and a true density of 2.25 g/cm.sup3. or higher.

10. . . . electrode according to claim 9, wherein the carbonaceous material is graphitized powders or carbonaceous powders which have a plane space d002 of the (002) plane less than 0.337 nm in the X-ray wide angle diffraction method, a crystallite size (Lc) of 90 nm or higher, and an average particle size of 10 µm or higher.

L118 ANSWER 11 OF 13 EUROPATFULL COPYRIGHT WILA on STN

PATENT APPLICATION - PATENTANMELDUNG - DEMANDE DE BREVET

AN 782207 EUROPATFULL ED 19970720 EW 199727 FS OS Full-text

TIEN Nonaqueous type secondary battery.

IN Yamada, Kazuo, Kongo-ryo, 192-1, Hajikami, Shinjo-cho, Kitakatsuragi-gun, SHARP KABUSHIKI KAISHA, 22-22 Nagaike-cho Abeno-ku, Osaka-shi Osaka 545,

PI EP 782207 A1 19970702 PRAI JP 1995-336697 19951225 JP 1996-326371 19961206

ABEN A nonaquerous type secondary battery includes a working electrode containing graphite particles coated with less crystallized carbon and a nonaquerous electrolyte, which solution contains at least ethylenecarbonate and propylene carbonate. <image>

CLMEN. . . third solvent less viscous than PC and EC; and
the graphite particles have an interlayer spacing d.sub002. between
the (002) planes of 0.335 to 0.340 nm, a crystallite thickness
Lc in a direction orthogonal to the (002) plane of not less
than 10 nm, a crystallite thickness La in a direction orthogonal to
(110) plane of not. . . than 10 nm, and a ratio R of argon laser
Raman scattering peak intensities at about 1360 cm.sup-1. to about
1580 cm.sup-1. of not greater than 0.4.
2. The nonaqueous type secondary battery as recited in claim 1, wherein

- 2. The nonaqueous type secondary battery as recited in claim 1, wherein the interlayer spacing d.sub002. between the (002) planes of said graphite particles is in the range from 0.335 nm to 0.340 nm, and the thickness of crystallite Lc in the direction orthogonal to the (002) plane is not less than 10 nm, and the thickness of crystallite La in the direction orthogonal to (110) plane.
 3. . . intensity ratio R of a peak in the vicinity of 1360 cm.sup-1. relative to a peak in the vicinity of 1580 cm.sup-1. in argon laser Raman scattering, and the intensity ratio R of said graphite particles coated with less crystallized carbon is larger than 0.4.
- 6. . . . less crystallized carbon have a ratio R of argon laser Raman scattering peak intensities at about 1360 cm.sup-1. to about 1580 cm.sup-1. of greater than 0.4.

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PATENT APPLICATION - PATENTANMELDUNG - DEMANDE DE BREVET
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495613 EUROPATFULL UP 20000709 EW 199230 FS OS STA B Full-text
AN
       Lithium secondary battery and carbonaceous material useful therein.
TIEN
       Takami, Norio, c/o Intellectual Property Division, Toshiba Corporation,
ΤN
       KABUSHIKI KAISHA TOSHIBA, 72, Horikawa-cho Saiwai-ku, Kawasaki-shi
PA
       EP 495613
                           A2 19920722
PΙ
                              19910114
       JP 1991-2859
PRAI
         JP 1991-110607
                                19910515
         JP 1991-187999
                                19910729
                                19910731
         JP 1991-213194
```

ABEN A lithium secondary battery, comprising:

- a vessel;
- a positive electrode containing an active material housed in the vessel;
- a lithium ion conductive electrolyte in the vessel, and
- a negative electrode arranged in the vessel containing carbonaceous material spherical particles as active material that absorbs and discharges lithium ions, the carbonaceous material spherical particles containing a graphite-like layered structure part and a turbulence-layered structure part, fine structures of the carbonaceous material spherical particle being arranged in point-orientation.

There is also provided a process for making carbonaceous material for a negative electrode of a lithium secondary battery comprising the step of heat-treating for carbonizing a spherical particle or a fibre, the heat-treating step including one of the steps of carbonizing a mesophase small spherical particle or a mesophase pitch fibre in an inert gas or a vacuum at a temperature of more than 1200°C up to 2500°C. <image>

DETDEN As the index to specify the graphite-like layered structure of the carbonaceous material, the parameters of interplanar spacing of (002) surface (d.sub0..sub0..sub2.) and mean size of the crystal lattice along the c-axis (Lc) are used effectively. Both of these parameters can be measured by means of X-ray diffraction....

CLMEN 2. A battery as claimed in claim 1, wherein the mean value of the (002) face distance (d.sub0..sub2.) in the carbonaceous

material spherical particle is 0.337 nm to 0.380 nm.

- 3. A battery as claimed in claim 1 or 2, wherein the mean size of the crystal lattice (Lc) along the C-axis in the spherical particle is 1 nm to 25 nm.
 - 3. A battery as claimed in claim 1 or 2, wherein the mean value of the (002) face distance (.supd.002) in the carbonaceous

material spherical particle is 0.337 nm to 0.380 nm.

- 4. . . is 0.5 to 1.5 where:
 - R.subl. is a peak value at 1360.supmin..supl. cm, and
 - R.sub2. is a peak value at 1580.supmin..sup1. cm.
- 4. A battery as claimed in any preceding claim, wherein the mean size of the crystal lattice (Lc) along the C-axis in
- the spherical particle is 1 nm to 25 nm.
- 5. . . a peak value in the region of 1360.sup-1. cm, and
 - R.sub2. is a peak value in the region of 1580.sup-1. cm.
- 6. A battery as claimed in any preceding claim, wherein the average
- size of the spherical particles is 0.5 μm to 100 $\mu m\,.$
- 7. A battery as claimed in any preceding claim, wherein the average
- size of the spherical particles is 0.5 μm to $\,$ 100 $\,\mu m$.
- 10. A battery as claimed in claim 9, wherein the mean value of the (
- 002) face distance (d.sub0..sub0..sub2.) in the carbonaceous
- material fibres is 0.337 nm to 0.380 nm.
- 10. A battery as claimed in claim 9, wherein the mean value of the (
- 002) face distance (.supd.002) in the carbonaceous
- material fibres is 0.337 nm to 0.380 nm.
- 11. A battery as claimed in claim 9 or 10, wherein the mean size of the crystal lattice (Lc) along the C-axis direction in the fibres is 1 nm to 25 nm.
- 12. . . is 0.5 to 1.5 where; R.subl. is a peak value at 1360.supmin..supl. cm, and R.sub2. is a peak value at 1580.supmin..supl. cm.

L118 ANSWER 13 OF 13 EUROPATFULL COPYRIGHT WILA on STN

PATENT APPLICATION - PATENTANMELDUNG - DEMANDE DE BREVET

339691 EUROPATFULL ED 20000917 EW 198944 FS OS STA B Full-text

TIEN Process for producing graphite films and fibers.

IN Murakami, Mutsuaki, 2297 (13-21), Miwa-cho Machida, Tokyo 194-01, JP PA Research Development Corporation of Japan, 5-2, Nagatacho 2-chome,

PI EP 339691 A2 19891102 PRAI JP 1985-115417 19850530

JP 1985-140207 19850628

Disclosed are a process for producing a graphite film and fiber, which comprises heat treating a film or fiber of at least one polymer selected from the group consisting of a polyoxadiazole, polybenzothiazoles, a polybenzobisthiazole, a polybenzoxazole, a polybenzobis.shy. oxazole and a polythiazole under tension at a temperature of 400° to 700°C in vacuo or in an inert gas, and then heat treating the film or fiber at a temperature of at least 1600°C in vacuo or in an inert gas, thereby graphitizing the film or fiber, and a process for producing a graphite film, which comprises heat treating a film of at least one polymer selected from the group consisting of a polyoxadiazole, polybenzothiazoles, a polybenzobisthiazole, a polybenzoxazole, a polybenzobis.shy. oxazole, poly(pyromellitic acid imide), poly(m-phenylene isophthalic acid amide), poly(m-phenylenebenzobisimidazole) and a polythiazole at a temperature of at least 1800°C in vacuo or in an inert gas, then impregnating the film with a binder component, and heat treating the impregnated film at a temperature of not more than 1400°C.

According to the present invention, almost perfect graphite films and fibers can be extremely easily obtained at a lower temperature. Further, graphite films excellent in electric conductivity and mechanical properties can be produced.

PRAI JP 1985-115417 19850530 JP 1985-140207 19850628 PRAI JP 1985-115417 19850530 JP 1985-140207 19850628

DETDEN

In order to indicate the extent of graphitization, parameters measured by X-ray diffraction such as lattice constant, crystallite size in the direction of C-axis and the like, and degree of graphitization calculated therefrom are usually used. Also, the value of electric conductivity is often utilized. The lattice constant is calculated from the position of the (002) diffraction line of X-ray. It is shown that the closer the constant is to 0.6708 nm (6.708A) which is the lattice constant of natural monocrystal graphite, the more the graphite structure is developed. The crystallite size in the direction of C-axis is calculated from the half breadth of the (002) diffraction line. It is shown that the larger the value thereof is, the more the planar structure of graphite is developed. The craystallite size of natural monocrystal graphite is at least 100 nm (1000A). The degree of graphitization is calculated from the crystal face spacing d.sub0..sub2.) by the method described in the literature. . .

Crystallite size (L.subc.) is calculated from the

half breadth (β) of the diffraction line obtained by correcting the (002) diffraction line, according to the following relational formula: <image> where K is the shape factor. The . . . by the Cu K α -ray using a Phillips Model PW-1051 X-ray diffractometer. The value of C.subo. is calculated from the (002) diffraction line which appears in the neighborhood of 2.thetav. equal to 26° to 27° by using the following Bragg's formula: . .

DIAMOND FILMS AND COATINGS

Development, Properties, and Applications

Edited by

Robert F. Davis

North Carolina State University

Department of Materials Science and Engineering
Raleigh, North Carolina



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techniques, the inelastic process exploited results from the same physical entity, the vibrating dipole, with complementary selection rules applied for Raman and IR activities. Both techniques have found tremendous uses in the characterization of CVD diamond films due to their ability to distinguish different chemical bonding types. Particularly in this respect, Raman spectroscopy has become the most popular and powerful technique in the analysis of the quality of CVD diamond films.

2.1 Raman Spectroscopy

Raman spectroscopy is one of many light-scattering phenomena. All these phenomena originate from the principle that the intensity of a beam of light decreases measurably when it passes through a nonabsorbing medium. The Raman effect belongs to the class of molecular-scattering phenomena. It is based on inelastic light-scattering arising from the interactions of photons with lattice vibrations or phonons. A laser tuned to a single line is used to excite the Raman scattering. The phonons are coupled to the photons through the polarization induced in the crystal by the electric field of the intense light beam. They are related by the polarizability as:

$$P = \alpha E$$

where P is the induced electric moment, E is the electric field and α is the polarizability. A lattice vibration is Raman active when the vibration changes the polarizability (1)(2). Some photons will be emitted from the induced oscillating dipoles which are either of the same frequency as the incident beam (elastic Rayleigh scattering) or have been frequency shifted by an amount equal to the vibrational frequency of the lattice (inelastic Stokes or anti-Stokes scattering):

$$P = E_0 \alpha_0 \cos(2\pi v_0 t) + \frac{1}{2} E_0 \sum_{n} \left[\cos 2\pi (v_n - v_n) t + \cos 2\pi (v_n + v_n) t\right]$$

where E_o is the electric field of incident light, v_o is the frequency of the incident light, v_n is the phonon frequency, α_n represents the polarizability as a function of the vibration mode, and t is the time. The shifted frequency is the Raman scattering which was named for Sir C. V. Raman, an Indian Nobel laureate, who discovered the effect in 1928 (3). The Stokes scattering (the normal Raman effect) is produced when energy is extracted from the light beam to the crystal and sets it into vibration, whereas the anti-Stokes

scattering arises from the annihilation of the existing thermally-excited vibration. The vibrational modes are dependent on the atomic bonding in the solid. Therefore, Raman spectra can be used to interpret the structures in solids.

Raman scattering has been very useful for studying the chemistry and physics of carbon, particularly of CVD diamond films (4)(5). It is very sensitive to the nature of the carbon bonding. Therefore, it is able to distinguish various types of carbon: diamond, graphite, amorphous carbon and hydrogenated carbon. It has far exceeded other techniques in popularity for this purpose. The intense first order Raman peak for diamond is located at 1332 cm⁻¹, and a second order feature centered at 2458 cm⁻¹ is often continuous and similar to the vibrational density of states (6). For highly oriented pyrolytic graphite, the first and second order peaks are located at 1580 cm⁻¹ and 3240 cm⁻¹, respectively (7). An additional peak at 1355 cm⁻¹ is observed for microcrystalline graphite which is related to the small domain size causing the momentum selection rules of the Raman scattering process to be relaxed (8). For amorphous carbon, there are two broad band features at approximately 1550 cm⁻¹ and 1355 cm⁻¹ (5)(9)(10). If the amorphous carbon is hydrogenated, the broad band at 1355 cm⁻¹ becomes a shoulder of the 1550 cm⁻¹ band (9). Since the Raman scattering efficiency for graphite is much greater than for diamond (11), small amounts of graphitic carbon co-deposited in CVD diamond films can readily be detected. Thus, if one is interested in a fast, sensitive and qualitative test for the quality of a film in terms of the bonding types, Raman spectroscopy is an excellent choice. Furthermore, information about domain (crystal) size, stress state and structural perfection can be obtained, because they cause broadening and shifts of the Raman peaks. However, the incorporation of low concentrations of sp^2 or π -type bonding may destroy any evidence of diamond in a Raman spectrum due to the large differences in scattering cross-sections. Therefore, if a small amount of non-diamond component is added to the film, a complex situation may arise in the interpretation of the Raman spectra. For example, in the authors' laboratory, certain films displaying mostly an sp² peak in the Raman spectra with only minor evidence of a diamond peak have been shown to yield EELS (electron energy loss spectroscopy) spectra essentially identical to diamond. Unfortunately, the exact "small amount" of the graphitic component in the film which is sufficient to distort the Raman spectra is not currently known.

Typical examples of Raman spectra for diamond films deposited under different conditions are shown in Fig. 1. For films deposited under optimal

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conditions, the spectrum is dominated by a sharp feature at 1332 cm⁻¹ which indicates the presence of crystalline diamond (Fig. 1a). A significant broad feature centered at ~1500 cm⁻¹ is observed in addition to the 1332 cm⁻¹ diamond signature for films deposited at non-optimized conditions (Fig. 1b). The intensity of this broad feature in CVD diamond can be fifteen times as strong as the peak intensity of pure graphite or microcrystalline graphite (12). This feature has been attributed to the presence of disordered or amorphous sp² carbon, although this assignment has not been universally accepted. As films become less like true diamond and more similar to "diamond-like" or amorphous carbon films (for example, as methane concentration increases in the feed gas during the deposition), this peak increases, and the 1332 cm⁻¹ peak decreases or even disappears as shown in Fig. 1c. Furthermore, a new feature at 1140 cm⁻¹ has also been observed (4). This new feature is still quite controversial and not well understood. It increases as the size of diamond crystallites decreases and has been observed most strongly for the diamond deposited at the beginning of a growth experiment (i.e., during the nucleation and initial growth phase). Nemanich et al. (4) indicated that the 1140 cm⁻¹ mode is at a frequency similar to that proposed for disordered or microcrystalline sp³ bonded carbon. Therefore, it is attributed to the small crystal sizes and/or disordered structure of diamond similar to the assignment of the 1355 cm⁻¹ peak to microcrystalline graphite. An important aspect which should be noted from the comparison of the different spectral signatures is that all features associated with the sp³ diamond bonding occur at frequencies lower than 1332 cm⁻¹, whereas the peaks due to sp² or graphitic bonding occur at higher frequencies than 1332 cm⁻¹. This is because the bond between sp² carbon is stronger than the sp³ carbon.

bonding in a carbon film via Raman spectroscopy. It would seem that if the relative scattering strengths are known, then it would be straightforward to determine the relative amounts of diamond and graphite in a "composite" CVD diamond film, assuming that the relative intensities of the two are directly related to the relative volume fractions of diamond and graphite present. Unfortunately, there are actually two important parameters related to the bonding structure which can affect the absolute Raman intensity: the scattering cross-section and the absorption coefficient. The absolute Raman cross-sections for diamond to graphite have been reported to be about 1:50 per unit volume (11) or 1:100 in terms of scattering per nearest-neighbor bond (1:75 per carbon atom) (12). On the other hand, graphite is highly absorbing, and diamond is effectively transparent in the visible range.

If samples containing graphite and diamond regions are illuminated with visible light, they will not be uniformly sampled. The transparent regions will be totally illuminated while only the surface of the absorbing regions will be measured. The effect of different absorptions becomes important when the domain size of the absorbing regions (graphite) is equal to or larger than the absorption length in graphite (~20 nm). Therefore, both concentrations and crystallite sizes of graphite have significant effects on the resulting Raman spectra. For CVD diamond, the size effect can be ignored for films in which there is no microcrystalline graphitic component. Films produced at optimal conditions seem to fulfill this requirement. In contrast, films produced at non-optimized conditions (for example, the methane concentration in hydrogen greater than 2.0%) contain features attributable to microcrystalline graphite, and quantitative analysis of these films may require a correction due to the domain size. Other considerations related to the quantitative analysis of sp³/sp² bonding include (12)(13): accounting for the anomalously strong Raman intensity of the sp² region at 1500 cm⁻¹ (a model of the sp² bonding configurations in which the π bonds in the graphitic regions are localized or attached to the sp³ sites has been proposed by Shroder et al. to account for these features at ~1550 cm⁻¹) (12); considering the effect of crystallographic orientations on the intensity of the diamond Raman line (especially in the case of microfocus Raman spectroscopy); separating the photoluminescence background and accurately determining the integrated area of the spectral features (this requires careful spectroscopy and computer deconvolution); and determining the relations between the peak intensity and the peak width. Therefore, to obtain a quantitative analysis of the relative percentage of sp3 to sp2 bonded carbon, not only the exact amount and nature of the sp² regions are important, but also their distribution within the crystals and the domain sizes of the sp2 regions. It is believed that quantification of the Raman results will be a high priority. Continuing efforts toward quantification of sp³/sp² in CVD diamond films via Raman spectroscopy are currently underway.

2.2 Infrared Spectroscopy

IR spectroscopy is a complementary technique to Raman spectroscopy. The selection rule for IR active vibration modes is that the vibration produces a finite change in the existing dipole moment (2), as opposed to the change of polarizability for Raman active vibration modes. That is, only transitions involving vibrational states coupled by a dipole operator can be observed by IR spectroscopy. Not all vibrational modes lead to a change of electric dipole moment, and consequently they will not be IR active. The

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HANDBOOK OF CARBON, GRAPHITE, DIAMOND AND FULLERENES

Properties, Processing and Applications

by

Hugh O. Pierson

Consultant and Sandia National Laboratories (retired)
Albuquerque, New Mexico

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Description:	This book is a review of the science and technology of the element carbon and its allotropes: graphite, diamond and the fullerenes. This field has expanded greatly in the last three decades stimulated by many major discoveries such as carbon fibers, low-pressure diamond and the fullerenes. The need for such a book has been felt for some time. These carbon materials are very different in structure and properties. Some are very old (charcoal), others new (the fullerenes). They have different applications and markets and are produced by different segments of the industry.

Graphite Structure and Properties

1.0 THE STRUCTURE OF GRAPHITE

1.1 General Considerations and Terminology

The origin of the word "graphite" is the Greek word "graphein" which means "to write". Indeed, graphite has been used to write (and draw) since the dawn of history and the first pencils were manufactured in England in the 15th century. In the 18th century, it was demonstrated that graphite actually is an allotrope of carbon.

Graphite is remarkable for the large variety of materials that can be produced from its basic form such as extremely strong fibers, easily sheared lubricants, gas-tight barriers, and gas adsorbers. All these diverse materials have one characteristic in common: they are all built upon the trigonal sp² bonding of carbon atoms.

Strictly speaking, the term "graphite" by itself describes an ideal material with a perfect graphite structure and no defects whatsoever. However, it is also used commonly, albeit incorrectly, to describe graphitic materials. These materials are either "graphitic carbons", that is, materials consisting of carbon with the graphite structure, but with a number of structural defects, or "non-graphitic carbons", that is, materials consisting of carbon atoms with the planar hexagonal networks of the graphite structure, but lacking the crystallographic order in the c direction. [1] This is a fundamental difference and these two groups of materials are distinct in many respects, with distinct properties and different applications.

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As a reminder and as mentioned in Ch. 1, the term "carbon" by itself should describe the element and nothing else. To describe a material, it is coupled with a qualifier, such as "carbon black," "activated carbon," "vitreous carbon," "amorphous carbon," and others.

1.2 Structure of the Graphite Crystal

Graphite is composed of series of stacked parallel layer planes shown schematically in Fig. 3.1, with the trigonal sp² bonding described in Ch. 2, Sec. 4.0. In Fig. 3.1 (and subsequent figures of the carbon structure), the circles showing the position of the carbon atoms do not represent the actual size of the atom. Each atom, in fact, contacts its neighbors.

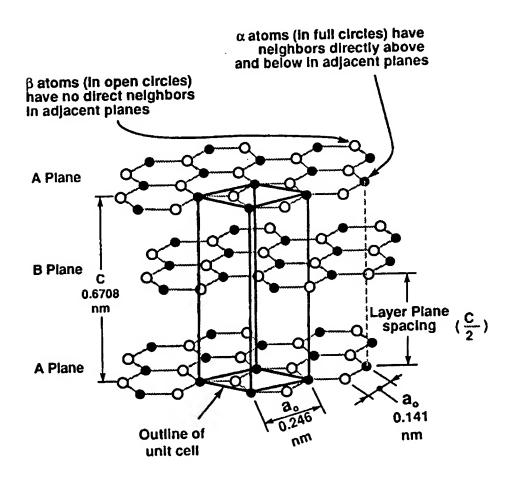


Figure 3.1. Crystal structure of graphite showing ABAB stacking sequence and unit cell.

Within each layer plane, the carbon atom is bonded to three others, forming a series of continuous hexagons in what can be considered as an essentially infinite two-dimensional molecule. The bond is covalent (sigma) and has a short length (0.141 nm) and high strength (524 kJ/mole). The hybridized fourth valence electron is paired with another delocalized electron of the adjacent plane by a much weaker van der Waals bond (a secondary bond arising from structural polarization) of only 7 kJ/mol (pi bond). Carbon is the only element to have this particular layered hexagonal structure.

The spacing between the layer planes is relatively large (0.335 nm) or more than twice the spacing between atoms within the basal plane and approximately twice the van der Waals radius of carbon. The stacking of these layer planes occurs in two slightly different ways: hexagonal and rhombohedral.

Hexagonal Graphite. The most common stacking sequence of the graphite crystal is hexagonal (alpha) with a -ABABAB- stacking order, in other words, where the carbon atoms in every other layer are superimposed over each other as shown in Fig. 3.1.

Atoms of the alpha type, which have neighbor atoms in the adjacent planes directly above and below, are shown with open circles. Atoms of the beta type, with no corresponding atoms in these planes, are shown with full circles. A view of the stacking sequence perpendicular to the basal plane is given in Fig. 3.2.

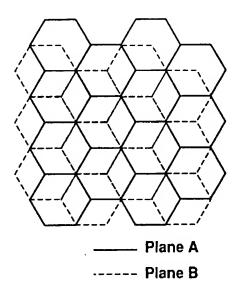


Figure 3.2. Schematic of hexagonal graphite crystal. View is perpendicular to basal plane.

Other characteristics of the graphite crystal are the following;

- The crystallographic description is given by the space group D_{6H}-P₆₃/mmc.
- The crystal lattice parameters, i.e., the relative position of its carbon atoms (along the orthohexagonal axes) are: $a_0 = 0.245$ nm and $c_0 = 0.6708$ nm.
- The common crystal faces are {0002}, {1010}, {1011} and {1012}.
- The crystal cleavage is {0002} with no fracture.
- The crystal is black and gives a black streak.
- Hexagonal graphite is the thermodynamically stable form of graphite and is found in all synthetic materials.

Rhombohedral Graphite. The other graphite structure is rhombohedral with the stacking order -ABCABCABC-. The carbon atoms in every third layer are superimposed. The crystallographic description is given by the space group D_{3d}^5 -R3m. The crystal lattice parameters are: $a_0 = 0.2256$ nm and $c_0 = 1.006$ nm. A view of the stacking sequence perpendicular to the basal plane is given in Fig. 3.3.

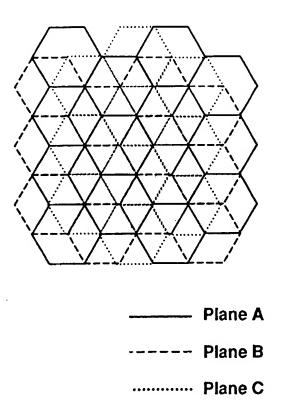


Figure 3.3. Schematic of rhombohedral graphite crystal. View is perpendicular to basal plane.

Rhombohedral graphite is thermodynamically unstable, and can be considered as an extended stacking fault of hexagonal graphite. It is never found in pure form but always in combination with hexagonal graphite, at times up to 40% in some natural and synthetic materials. It usually reverts to the hexagonal form during heat treatment above 1300°C. It should be noted that in both structures, hexagonal and rhombohedral, no basal plane lies directly over another one.

2.0 THE VARIOUS POLYCRYSTALLINE FORMS OF GRAPHITE

The ideal hexagonal graphite structure described above is composed of theoretically infinite basal planes with perfect -ABAB- stacking, with no defects whatsoever. Such an ideal structure is, of course, never found, either in natural or synthetic graphite.

2.1 Polycrystalline Graphite

Graphite materials, such as pyrolytic graphite, carbon-fiber—carbon-matrix composites (carbon-carbon), vitreous carbon, carbon black, and many others, are actually aggregates of graphite crystallites, in other words, polycrystalline graphites. These crystallites may vary considerably in size. For instance, the apparent crystallite size perpendicular to the layer planes (L_c) of some vitreous carbons may be as small as 1.2 nm which is the length of a few atoms, or up to 100 nm found in highly ordered pyrolytic graphites (see Ch. 7). The layer planes may or may not be perfectly parallel to each other, depending whether the material is graphitic or non-graphitic carbon.

The aggregates of crystallites also have widely different sizes and properties. Some, such as soot, are extremely small and contain only a few small crystallites. In such cases, the properties are mostly related to the surface area (see Ch. 10).

Other aggregates may be relatively large and free of defects and essentially parallel to each other, in which case the structure and its properties closely match those of the ideal graphite crystal. Such large aggregates are often found in pyrolytic graphite (see Ch. 7).

In other aggregates, the crystallites have an essentially random orientation. This occurs in turbostratic (i.e., showing no evidence of three-dimensional order) or amorphous carbon shown in Fig. 3.4. In such cases, the bulk properties are essentially isotropic.

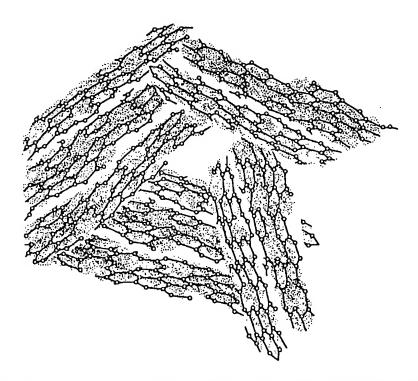


Figure 3.4. Structure of turbostratic graphite. Note lattice defects and vacancies.

2.2 Crystallite Imperfections

Within each crystallite, a varying number of imperfections may be found as shown in Figs. 3.4 and 3.5. These include:

- Vacancies, when lattice sites are unfilled indicating a missing atom within a basal plane
- Stacking faults when the ABAB sequence of the layers planes is no longer maintained
- Disclination when the planes are no longer perfectly parallel

Other crystalline imperfections likely caused by growth defects are screw dislocations and edge dislocations (Fig. 3.6). The presence of these imperfections may have a considerable influence on the properties of the bulk material.

Thus in each graphitic material, the size, shape, and degree of imperfection of the basic crystallite, the general orientation of these crystallites, as well as the bulk characteristics such as porosity and amount of impurities, may vary considerably from one material to another. As a result, the properties of these various materials may show considerable differences.

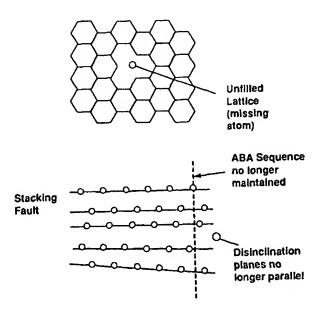


Figure 3.5. Schematic of crystallite imperfections in graphite showing unfilled lattice, stacking fault, and disinclination.

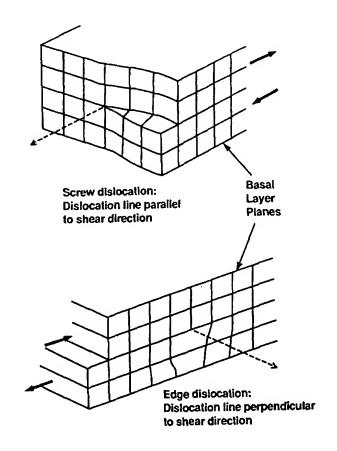


Figure 3.6. Shear dislocations in a graphite crystal.

An important implication is that, whereas material differences in the various carbon materials were originally ascribed to the presence (or absence) of an "amorphous" component (as in lampblack for instance), a more realistic approach is to relate these differences to the size and orientation of the graphite crystallites.

The specific structure and properties of the different graphitic materials will be reviewed in detail in subsequent chapters.

3.0 PHYSICAL PROPERTIES OF GRAPHITE

The properties of the ideal graphite material, that is a material that most closely corresponds to an infinitely large graphite crystal, are reviewed in this section. Such a material does not exist in the real world and the properties given below are either calculated or based on the actual properties of graphite crystals closely approaching this ideal structure.

As already mentioned and as will be seen in later chapters, a wide range of materials comes under the heading of carbon or graphite and these materials often have properties that are much different from those of the ideal graphite crystal. Obviously it is necessary to define the material accurately when speaking of the properties of "carbon" or "graphite".

3.1 Anisotropy of the Graphite Crystal

The peculiar crystal structure of graphite results in a considerable anisotropy, that is the properties of the material may vary considerably when measured along the *ab* directions (within the plane) or the *c* direction (perpendicular to the planes). Such anisotropy, especially in electrical and thermal properties, can often be put to good use as will be seen in later chapters.

3.2 Summary of Physical Properties

The physical properties of graphite are summarized in Table 3.1. It should be stressed that to obtain accurate measurements of the properties of materials much above 3000 K is a trying task. In the case of graphite, many of these measurements are based on carbon-arc experiments which are difficult to perform and interpret. The results must be viewed accordingly and some of these results and conclusions are still controversial.

Table 3.1. Physical Properties of Graphite

Crystalline form: hexagonal

Lattice parameters: $a_0 = 0.246 \text{ nm}$

 $c_0 = 0.671 \text{ nm}$

Color: Black

Density at 300 K, 1 atm: 2.26 g/cm³ (see below)

Atomic volume: 5.315 cm³/mol

Sublimation point at 1 atm (estimated): 4000 K

(see below)

Triple point (estimated): 4200 K (see below)

Boiling point (estimated): 4560 K

Heat of fusion: 46,84 kJ/mol

Heat of vaporization to monoatomic gas (estimated):

716.9 kJ/mol (see below)

Pauling electronegativity: 2.5

3.3 Density

The density of the perfect crystal listed in Table 3.1 is the theoretical density. Most graphite materials will have lower densities due to the presence of structural imperfections such as porosity, lattice vacancies and dislocations.

With the exception of boron nitride, graphite materials have a lower density than all other refractory materials as shown in Table 3.2. This is a advantageous characteristic especially in aerospace applications.

3.4 Melting, Sublimation, and Triple Point

The melting point of a crystalline material such as graphite is the temperature at which the solid state is in equilibrium with the liquid at a given pressure. "Normal" melting point occurs at a pressure of one atmosphere. Graphite does not have a normal melting point since, at one atmosphere, it does not melt but sublimes when the temperature reaches approximately 4000 K. To observe melting, a pressure of 100 atm and a temperature of 4200 K are necessary.

	g/cm ³
Graphite	2.26
Molybdenum	10.22
Rhenium	21.04
Tantalum	16.6
Tungsten	19.3

Table 3.2. Density of Some Refractory Materials

Titanium diboride

Hafnium carbide

Tantalum carbide

Aluminum oxide

Zirconium oxide

Boron nitride

The triple point (where all three phases, solid, liquid, and gas, are in equilibrium) is achieved, by recent estimates, at a temperature of 4200 K and a pressure of 100 atm, as shown in the vapor-pressure curve of Fig. 3.7.^{[3]-[5]} A great deal of uncertainty still remains regarding these values of pressure and temperature, reflecting in part the difficulty of conducting experiments under such extreme conditions.

4.50 12.20

13.9

2.25

3.97

5.89

The onset of sublimation and the melting temperatures are apparently close. At temperatures above that of the triple point and at pressures of argon greater than 100 atm, a mixture of solid and liquid carbon is detected.

Graphite can thus be considered the most refractory of all the elements, tungsten being second-best with a melting point of 3680 K. However hafnium carbide (HfC) and tantalum carbide (TaC) are reported to have higher melting points (approximately 4220 K and 4270 K respectively) and are the most refractory of all materials.^[6]

3.5 Heat of Vaporization

The heat of vaporization of graphite is higher than that of many metals as shown in Table 3.3.^{[7][8]} Reported values show considerable differences.

The large amount of energy required to vaporize graphite is used to good advantage in the design of ablative structures such as nose cones and rocket nozzles (see Ch. 7 and 9).

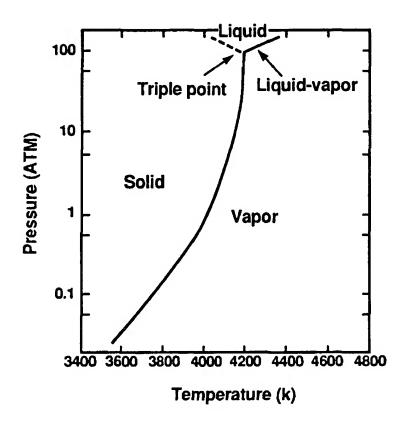


Figure 3.7. Vapor pressure and triple point of graphite. [3][4]

Table 3.3. Heat of Vaporizaton of Selected Elements at Boiling Point

	(kJ/mol)
Graphite	355.8 - 598.2
Molybdenum	598.0
Copper	300.3
Iron	349.6
Nickel	370.4
Tungsten	824.0
Silver	250.5

4.0 THERMAL PROPERTIES OF GRAPHITE

4.1 Summary of Thermal Properties

The physical properties reviewed in the previous section are essentially unaffected by the size and orientation of the crystallites in the aggregate (with the exception of density). As a result, they can be considered valid for all forms of graphite. This is no longer true for some of the properties listed in this and the following sections, and these properties may vary considerably depending on crystallite size and orientation and other factors related to the processing conditions.

The thermal properties are summarized in Table 3.4. Whenever possible, a range of property values is given. More detailed values are given in subsequent chapters.

Table 3.4. Theoretical Thermal Properties of Graphite

Heat of combustion ΔHco @ 25°C and constant pressure to form CO ₂ gas, kJ/mol	393.13
Standard entropy S° at 25°C, J/mol·K	5.697 - 5.743
Entropy ΔS ₂₉₈ , J/mol·K	152.3
Enthalpy ΔH298, kJ/mol	716.88
Specific heat @ 25°C, kJ/kg·K (see below)	0.690 - 0.719
Thermal conductivity @ 25°C, W/m·K (see beloab direction c direction	ns 398
Thermal expansion: see below	

4.2 Heat Capacity (Specific Heat)

The molar heat capacity (specific heat) of graphite is reported as 8.033 - 8.635 J/mol·K at 25°C.^{[8]-[10]} As with all elements, it increases with temperature, with the following relationship (T in deg K).^[11]

$$C_p = 4.03 + (1.14 \times 10^{-3})T - (2.04 \times 10^5)/T^2$$

The specific heat increases rapidly with temperature, up to 1500 K where it levels off at approximately 2.2 kJ/kg·K as shown in Fig. 3.8.^[3] It is believed to be relatively insensitive to the differences between the various grades of synthetic graphite, and the spread of values found in the literature may be attributed to experimental variations. The average value is compared to that of selected other elements in Table 3.5. As can be seen, it is higher than most metals.

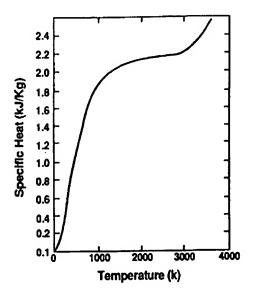


Figure 3.8. Specific heat of graphite vs. temperature at one atmosphere. [3]

Table 3.5. Specific Heat of Selected Elements

	C _p at 25°C and 1 atm. (kJ/kg·K)
Graphite	0.690 - 0.719
Diamond	0.502 - 0.519
Boron	1.025
Aluminum	0.900
Titanium	0.523
Copper	0.385
Niobium	0.263
Rhenium	0.242
Tungsten	0.130
Water	4.186

4.3 Thermal Conductivity

The thermal properties of conductivity and expansion are strongly influenced by the anisotropy of the graphite crystal. The thermal conductivity (K) is the time rate of transfer of heat by conduction. In graphite, it occurs essentially by lattice vibration and is represented by the following relationship (Debye equation):

Eq. (1)
$$K = bC_p vL$$

where: b = a constant

C = specific heat per unit volume of the crystal

v = speed of heat-transporting acoustic wave (phonon)

L = mean free path for wave scattering

In a polycrystalline materials, the waves (phonon, i.e., quantum of thermal energy) are scattered by crystallite boundaries, lattice defects, and other phonons. Little of this occurs in a perfect or near-perfect graphite crystal in the basal plane and, as a result, the factor L is high and thermal conductivity is high in the ab directions. However, in the direction perpendicular to the basal plane (c direction), the conductivity is approximately 200 times lower since the amplitude of the lattice vibration in that direction is considerably lower than in the ab directions. These differences in vibration amplitude in the various crystallographic directions of graphite are shown in Fig. 3.9.[12]

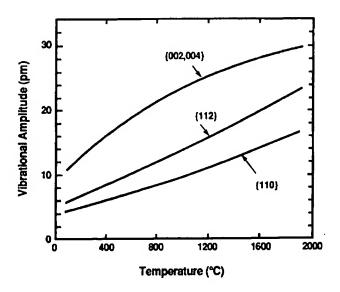


Figure 3.9. Thermal vibrational amplitude of graphite crystal in the {002,004}, {112}, and {110} directions.[12]

The thermal conductivity of a graphite crystal has been reported as high as 4180 W/m·K in the *ab* directions for highly crystalline, stress-annealed pyrolytic graphite.^[2] However, the average value for commercial pyrolytic graphite is considerably smaller (~390 W/m·K).^[13] Still, this is a high value and graphite, in the *ab* directions, can be considered a good thermal conductor comparable to high-conductivity metals and ceramics as shown in Table 3.6. Graphite fibers from pitch precursor have high thermal conductivity up to 1180 W/m·K, nearly three times that of copper (see Ch. 8, Sec. 6).

Table 3.6. Thermal Conductivity of Selected Materials

,	W/m·K at 25°C
Pyrolytic graphite:	
ab directions	390
c direction	2
Graphite fiber (pitch-based)	1180
Diamond (Type II)	2000 - 2100
Silver	420
Copper	385
Beryllium oxide	260
Aluminum nitride	200
Alumina	25

The thermal conductivity in the c direction is approximately 2.0 W/m·K and, in that direction, graphite is a good thermal insulator, comparable to phenolic plastic.

The thermal conductivity of graphite decreases with temperature as shown in Fig. 3.10.^[14] In the Debye equation (Eq. 1), K is directly proportional to the mean free path, L, which in turn is inversely proportional to temperature due to the increase in vibration amplitude of the thermally excited carbon atoms. L becomes the dominant factor above room temperature, more than offsetting the increase in specific heat, C_p , shown in Fig. 3.8.

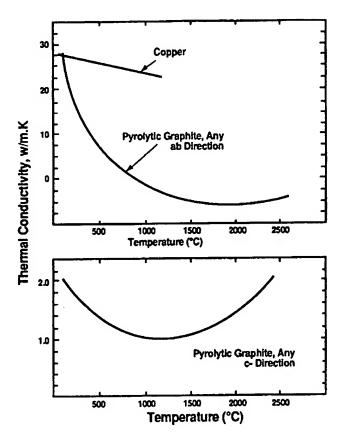


Figure 3.10. Thermal conductivity of graphite crystal in the ab and c directions. [14]

4.4 Thermal Expansion

The interatomic spacing between the carbon atoms of graphite (as with any other material) is a function of temperature. At 0 K (-273°C), these atoms have their lowest energy position or ground state (see Ch. 2, Sec. 4). The increased energy resulting from increasing temperature causes the atoms to vibrate and move further apart. In other words, the mean interatomic spacing increases and the result is thermal expansion.

This can be represented graphically in Fig. 3.11. As seen in this figure, the graphic relationship between interatomic spacing and energy has the configuration of a trough. This configuration changes with the strength of the atomic bond. In a strongly bonded solid such as graphite in the ab directions, the trough is deep, the amplitude of the vibrations is small and, during the outward motion of the atoms, the atomic bonds are not overstretched and, consequently, the dimensional changes remain small. When the atomic bond is weak such as in graphite in the c direction, the energy trough is shallow and the vibration amplitude and the dimensional changes are large. [15]

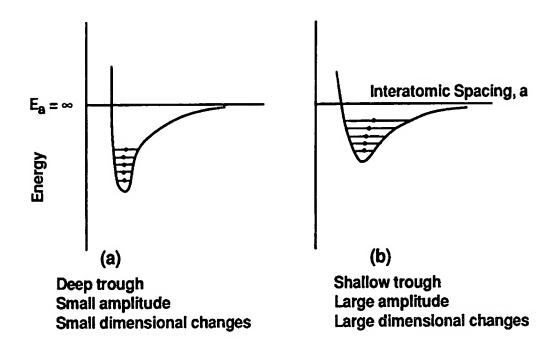


Figure 3.11. The energy trough of graphite in (a) ab directions and (b) c direction. [14]

As a result, the thermal expansion of the graphite crystal has a marked anisotropy. It is low in the *ab* directions (lower than most materials) but higher by an order of magnitude in the c direction, as shown in Fig. 3.12.[2][13][16]

The increase with temperature is not linear. In the c direction, it increases slowly and gradually. At 0°C, the coefficient of thermal expansion averages 25 x 10-6/°C and at 400°C, it reaches 28 x 10-6/°C. [2][14][17]

In the ab directions, the thermal expansion is actually negative up to approximately 400°C with a minimum at 0°C. It is possible that this observed negative expansion is due to internal stress (Poisson effect) associated with the large expansion in the c direction and it has been suggested that, if it were possible to measure the ab thermal expansion of a single atomic plane, this expansion would be positive. [18]

The large thermal expansion anisotropy often results in large internal stresses and structural problems such as delamination between planes as will be seen in Ch. 5, Sec. 3.

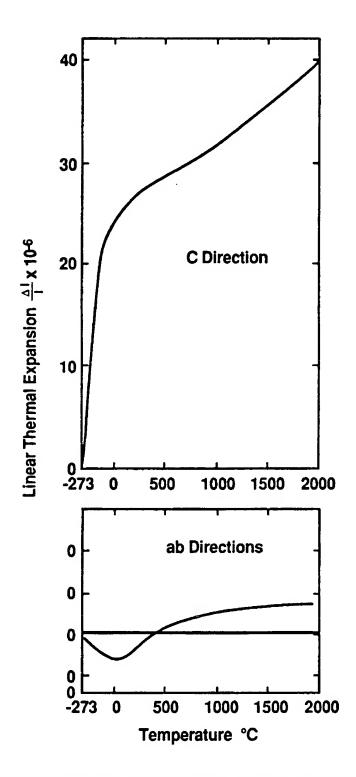


Figure 3.12. Thermal expansion of the graphite crystal in the ab and c directions. [2][3][15]

5.0 ELECTRICAL PROPERTIES OF GRAPHITE

5.1 Electrical Resistivity

In electrical conductors such as metals, the attraction between the outer electrons and the nucleus of the atom is weak; the outer electrons can move readily and, since an electric current is essentially a flow of electrons, metals are good conductors of electricity. In electrical insulators (or dielectrics), electrons are strongly bonded to the nucleus and are not free to move. [18][19]

Electrically, graphite can be considered as a semi-metal, that is a conductor in the basal plane and an insulator normal to the basal plane. Its atomic structure is such that the highest-filled valence band overlaps the lowest-empty conduction band by approximately 36 meV and the delocalized fourth-valence electrons form a partially-filled conduction band between the basal planes where they can moved readily in a wave pattern as they respond to electric fields. [20] Consequently, the electrical resistivity of graphite parallel to the basal planes (ab directions) is low and the material is a relatively good conductor of electricity.

In the c direction, the spacing between planes is comparatively large, and there is no comparable mechanism for the electrons to move from one plane to another, in other words, normal to the basal plane. As a result the electrical resistivity in that direction is high and the material is considered an electrical insulator. In some cases, it may be 10,000 times higher than in the ab directions. Often quoted resistivity values are 3000 x 10^{-6} ohm.m in the ab directions.

5.2 Resistivity and Temperature

The electrical resistivity of the graphite crystal in the *ab* directions increases with temperature, as does that of metals. This increase is the result of the decrease in the electron mean free path, in a mechanism similar to the increase in thermal conductivity reviewed above in Sec. 4.3.

The electrical resistivity in the c direction, however, decreases slightly with increasing temperature, possibly because electrons can jump or tunnel from one plane to another due to increased thermal activation.^[14]

6.0 MECHANICAL PROPERTIES OF GRAPHITE

As mentioned in Sec. 1.2, the bond between atoms within the basal plane of a graphite crystal is considerably stronger than the bond between the planes with an anisotropy ratio of approximately 75. This means that, while the strength in the ab directions is considerable, that in the c direction (interlaminar strength) is low and graphite shears easily between basal planes. The elastic constants are: $^{[17]}$

 $C_{11} = 1060 \text{ GPa}$ (a direction)

 $C_{33} = 36.5 \text{ GPa}$ (c direction)

 $C_{44} = 4.5$ GPa (parallel to the planes)

The Young's modulus of elasticity of the crystal varies up to two orders of magnitude with the direction. It is plotted in Fig. 3.13 as a function of the angle between the c direction and the direction of measurement.^[2]

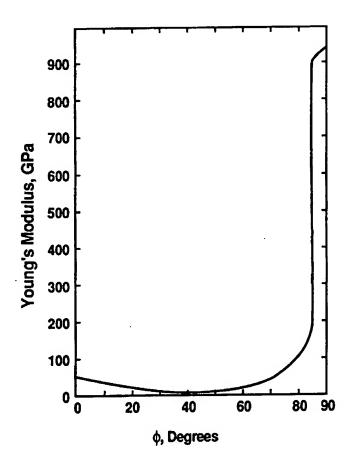


Figure 3.13. Young's modulus of graphite crystal as a function of angle (Θ) with c axis. [2]

It should be noted that such values are those of the ideal graphite crystal. The mechanical properties of "real" material, such as the molded graphite materials and pyrolytic graphite are considerably different since they are controlled by the dominant crystallite orientation, porosity, structural defects and other factors. The result is large variations in the range of these properties, depending on type of graphite and process. The mechanical properties of the various forms of graphite will be reviewed in detail in subsequent chapters.

7.0 CHEMICAL PROPERTIES

7.1 General Considerations

Pure graphite is one of the most chemically inert materials. It is resistant to most acids, alkalies and corrosive gases. However impurities are almost always present to some degree in both natural and artificial graphites and often have an important catalytic effect with resulting increase in the chemical reactivity.

The anisotropy of the graphite crystal is reflected in its chemical behavior. Reaction with gases or vapors occurs preferentially at "active sites", i.e., the end of the basal planes of the crystal which are the zigzag face {101} and the arm-chair face {112} as shown in Fig. 3.14, and at defect sites, such as dislocations, vacancies, and steps. Reaction with the basal plane surfaces is far slower. The reason is that the graphite crystal exhibits large differences in surface energy in the different crystallographic directions; these energies amount to 5 J/m² in the prismatic plane but only 0.11 J/m² in the basal plane. These differences account for the different rate of reaction, i.e., slow at the basal plane and rapid at the edge (or prismatic) surfaces found at the termination of the basal planes or at defects within the basal plane. Consequently, graphite materials with large crystals and few defects have the best chemical resistance.

The chemical reactivity is also appreciably affected by the degree of porosity, since high porosity leads to large increase in surface area with resulting increase in reactivity. Differences in reactivity between one form of graphite or another can be considerable. Obviously, high surface area materials such as activated carbon are far more reactive than dense, pore-free or closed-pore materials such as glassy carbon.

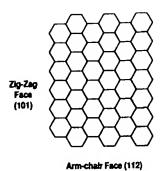


Figure 3.14. The faces of a graphite crystal.

Reactivity also generally increases with increasing temperature and, at high temperatures, graphite becomes far more reactive. For instance, above 450°C, it oxidizes readily with water, oxygen, some oxides, and other substances.

In this section, only the general chemical behavior of graphite will be considered. Reviews of the chemical reactivity of specific graphite materials will be given in subsequent chapters.

7.2 Summary of Chemical Properties

The general reactivity of graphite with the various classes of chemicals at ambient temperature is given in Table 3.7.^[22]

7.3 Reaction with Oxygen and Hydrogen

The one major exception to the generally excellent chemical resistance of graphite is poor resistance to the elements of Column VI (oxygen, sulfur, selenium and tellurium), particularly oxygen and oxygen compounds. Oxidation begins in air at 350 - 400°C. This low-temperature oxidation is in contrast with the behavior of other refractory materials: oxides, for instance, do not oxidize and many carbides form a protective oxide film on their surface that delays oxidation. In contrast, the oxides formed by the oxidation of graphite are gaseous (CO and CO₂) and offer no protection to the surface.

As mentioned in Sec. 7.1 above, the reaction rate is site preferential and oxidation is much higher along the zig-zag face of the crystal than it is along the armchair face (Fig. 3.14).^{[23][24]} Oxidation can be hindered by increasing the degree of graphitization and the crystallite size (thereby reducing the number of active sites).

Table 3.7. General Chemical Resistance of Graphite

	Resistance to Chemical Attack	
Acids and Acid Solutions		
 Mineral, non-oxidizing (HCI, HCN, H₃PO₄, 	HF) A	
■ Boiling H ₂ SO ₄	В	
 Mineral, oxidizing (Br₂, H₂Cr₂O₇, HNO₂, H 	CIO ₄) B	
 Inorganic salts, acid-forming (alum, BF₃, C NiCl₂, sulfates) 	CuCl ₂ , A	
 Organic, strong (pH <3) (acetic, carbolic, f maleic, oxalic, phenol, picric, salicic) 	formic,	
 Organic, weak (pH 3 - 7) (abietic, benzoic, cresol, lactic, palmitic) 	, citric, A	
 Organic salts, acid-forming (allyl, amyl chlethyl chlorides) Alkalis and Alkaline Solutions 	orides, A	
 Mineral, non-oxidizing (hydroxides, NaOH molten Mg, KOH) 	, hydrazine, A	
 Mineral, oxidizing (permanganate, perchlo perborates) 	rate, B	
 Inorganic salts, base forming (BaSH₂, bord phosphates, NH₂O₈, NaHSO₂, NaPO₃, Na 	_	
Organic, strong (pH >11) (ethanol amines	, pyridine) A	
Weak organic bases (pH 7 - 11) (aniline, s	soaps, urea) A	
Gases		
 Acid (BF₃, CO₂, Cl₂, HCl, HF, H₂S) 	Α	
 Alkaline (wet NH₃, steam to 300°C) 	Α	
 Anhydrous (dew point below 0°C) (NH₃, C F₂, H₂, HCl, HF, H₂S, methane, O₂ to 150 propane, SO₂) 	n	
 Liquefied (air, F₂, He, H₂, methane, N₂, O₃ 		
 Oxidizing (air above 250°C, F₂, N₂O₄, O₂ 	2)	
steam above 300°C)	C	
 Reducing (acetylene, ethane, methane) 	Α	
- 1 loadonia (door) lough of identity internation		

В
В
Α
Α
В
A
Α
Α
Α
A

The oxidation of graphite and the available protective coatings are reviewed in Ch. 9. The controlled oxidation of graphite, known as activation, results in open structures with extremely high surface area (see Ch. 5, Sec. 3.0).

Graphite does not react with hydrogen at ordinary temperatures. It reacts in the 1000 - 1500°C range to form methane (CH₄). The reaction is accelerated in the presence of a platinum catalyst. With nickel catalyst, the reaction begins at approximately 500°C.[25]

7.4 Reaction with Metals

Graphite reacts with metals that form carbides readily such as the metal of groups IV, V and VI.[12][25] These carbides are the so-called hard

carbides, which include the carbides of tungsten, molybdenum, titanium, vanadium and tantalum, as well as the non-metal carbides of silicon and boron.

Graphite reacts with iron to form iron carbide, Fe₃C, usually by the direct solution of carbon in the molten iron. Iron carbide may also be formed from the reaction of iron with a carbon-containing gas. This reaction is known as case-hardening.

The reaction rate of graphite with the precious metals, aluminum, and the III-V and II-VI semiconductor compounds is low and graphite is used successfully as a crucible to melt these materials.

Graphite reacts readily with the alkali metals: potassium, calcium, strontium, and barium. The atoms of some of these metals, notably potassium, can readily penetrate between the basal planes of the graphite crystal to form intercalated (or lamellar compounds) with useful properties. These compounds are reviewed in Ch. 10, Sec. 3.0.

7.5 Reaction with Halogens, Acids, and Alkalis

Like the alkali metals, some halogens, particularly fluorine, form intercalated compounds with graphite crystals. Reaction usually starts at 600°C. However, graphite does not react with chlorine at temperatures below that of the electric arc.

Oxidizing acids attack graphite to varying degree depending on the nature and surface area of the material. The reaction with concentrated nitric acid is as follows:

$$C + 4HNO_3 \rightarrow 2H_2O + 4NO_2 + CO_2$$

Depending on the reaction conditions, other products may be formed such as graphitic oxide ($C_7H_2O_4$), mellitic acid ($C_6(CO_2H)_6$) and hydrocyanic acid (HCN).^[7]

Another oxidizing acid that attacks graphite is boiling sulfuric acid. The simplified reaction is the following:

$$C + 2H_2SO_4 \rightarrow CO_2 + 2H_2O + 2SO_2$$

Other by-products may be formed such as benzoic acid, $C_6H_5CO_2H$, and mellitic acid, $C_6(CO_2H)_6$.

Hydrofluoric acid (HF) and the alkali hydroxides generally do not react with graphite.

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Other polymers, such as polyacrylonitrile (PAN), furfuryl alcohol, and phenolics, which have high molecular weight and a high degree of aromaticity (i.e., with many benzene rings), have a relatively high carbon yield. During carbonization, the polymeric chains do not break down and, unlike the aromatic hydrocarbons, do not go through a liquid or plastic stage. An exception to this is polyvinyl chloride (PVC) which carbonizes like an aromatic hydrocarbon. The carbonization sequence of specific polymers is described in subsequent chapters.

3.0 THE GRAPHITIZATION PROCESS

3.1 X-Ray Diffraction of Graphitic Materials

X-ray diffraction is a useful analytical technique to determine the changes in structure that occur during graphitization. A detailed analysis of this technique is given in Ref. 14. As with all crystalline materials, a sharp diffraction pattern is obtained with single-crystal graphite. This pattern is schematically shown in Fig. 4.5.^[2] Pronounced crystallinity is indicated by the development of the 002, 004 and 101 peaks.

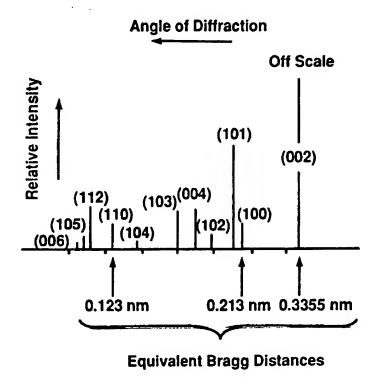


Figure 4.5. Schematic of diffraction patterns of hexagonal graphite.^[2]

The crystallite size, reviewed in Ch. 3, Sec. 2.1, is measured by x-ray diffraction from the breadth of the (110) and the (002) lines. The calculated value is not the actual size of the crystallite but is a relative value which is useful in determining the degree of graphitization of a carbon structure. The interlayer spacing is also determined from x-ray measurements and is another indication of the degree of graphitization.

3.2 Coke and Char

Graphitization can be defined as the transformation of a turbostratic-graphitic material (i.e., a "carbon") into a well-ordered graphitic structure. This occurs during heat treatment at temperatures often in excess of 2500°C.^{[2][4]} This structural change is accompanied by a large increase in the electrical and thermal conductivities of the material, an increase in its density which now approaches that of single crystal graphite, and a decrease in its hardness which facilitates machining into a finished product.

The degree of graphitization of carbon precursors such as those shown in Table 4.1 varies considerably, depending on whether a coke or a char is formed, as will be shown in the following sections.

3.3 Graphitization of Coke-Former Hydrocarbons

Cokes are formed by the carbonization of most aromatic hydrocarbons and a few polymers as mentioned above and are readily converted into a well-ordered graphite structure.

The coke-former aromatic hydrocarbons listed in Table 4.1 and shown in Fig. 4.2, i.e., naphthalene, anthracene, and acenaphtalene, are linear with a coplanar structure that has no preferred growth direction. This structural feature and the formation of a mesophase mentioned in Sec. 2.3 are the major factors in the easy conversion of the turbostratic structure into well-ordered graphite planes.^[13]

Coal-tar pitch is a mixture of these coke-forming aromatic hydrocarbons. As could be expected, it graphitizes readily and the degree of graphitization is a function of the ratio of aromatic to aliphatic hydrogen, known as hydrogen aromaticity (ratio of aromatic-hydrogen atoms to the total number of hydrogen atoms). In coal-tar pitch, this ratio varies between 0.3 and 0.9. The higher the ratio, the more graphitic the coke.^[12]

Some aromatic compounds do not form coke but char instead (see Sec. 3.5 below).

3.4 Graphitization Mechanism of Cokes

Graphitization occurs in a series of steps which begins as the increasing temperature passes the carbonization temperature, i.e., ~1200°C.^[13] Hydrogen, sulfur, and other elements, which might still be present after carbonization, are gradually removed and, as the temperature reaches 2000°C, essentially none remains.^[3]

Above 1800°C, the conversion from a turbostratic structure to a graphitic structure (shown in Figs. 3.4 and 3.2 of Ch. 3) begins slowly at first then more rapidly as the temperature passes 2200°C. The gradual graphitization of the structure is readily confirmed by x-ray diffraction (Fig. 4.5).

The crystallite size (L_c) increases from 5 nm, which is a typical size for turbostratic crystallites, to approximately 100 nm or more. At the same time, the interlayer spacing (d) is reduced from 0.344 nm to a minimum of 0.335 nm, which is the spacing of the graphite crystal.

In addition to the increase in L_c and the decrease in d, the graphitization mechanism includes the following steps: (a) removal of most defects within each graphite layer plane as well as between the planes, (b) gradual shifting and growth of the crystallites, (c) removal of cross-linking bonds, (d) evolution of the ABAB stacking sequence, and (e) shifting of carbon rings or single atoms to fill vacancies and eliminate dislocations (such vacancies and dislocations are shown schematically in Figs. 3.5 and 3.6 of Ch. 3).

Graphitization is accompanied by a weight loss, which is attributed to the removal of interlayer chemical species, mostly interstitial carbon. [15] Most graphitizable materials (cokes) require a temperature of 3000°C in order to reach full graphitization with a minimum value of the interlayer spacing, as shown in Fig. 4.6 and 4.7. [15][16] Also shown in Fig. 4.7 is the effect of the duration of graphitization (residence time). At 3000°C, full graphitization is usually obtained within 2 to 3 hours. Lower temperatures require considerably more time.

The process of graphitization can be accelerated by the presence of a metal catalyst or an oxidizing gas. In the latter case, obstacles to the ordering of the graphite layers, such as the more structurally disordered regions and the cross-linking bonds, are preferentially oxidized.

Graphitization can also be enhanced by the use of pressure. At high pressure, a greater degree of graphitization can be achieved at a given temperature than at atmospheric pressure. Likewise, high pressure results in a shorter heat-treatment time or a lower heat-treatment temperature.^[2]

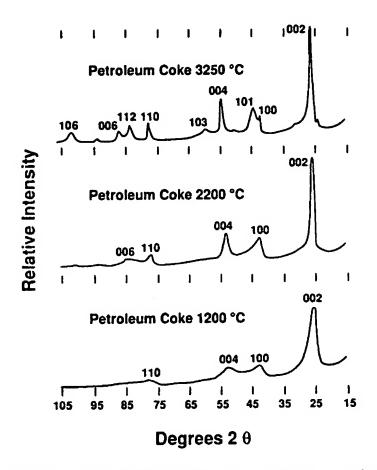


Figure 4.6. Diffraction patterns of petroleum coke as a function of graphitization temperature.^[15]

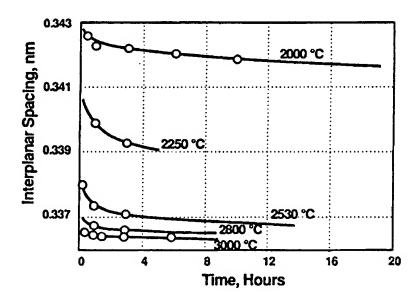


Figure 4.7. Basal plane spacing as a function of time for various temperatures of graphitization.^[16]

The kinetics of graphitization of cokes has been shown to be a growth process and not a nucleation-based process with usually a single-valued activation energy, reported at 962 ± 60 kJ/mol (230 ± 15 kcal/mol) in the 2300 - 2900°C temperature range for typical industrial cokes.^[17]

3.5 Graphitization of Chars

Graphitization of Aromatics. As mentioned above, not all aromatic hydrocarbons form coke. Some, such as phenanthrene and biphenyl, do not graphitize and are considered char formers. These compounds are branched aromatics (as opposed to the linear structure of the coke-former aromatics) with a preferred axis of growth as shown in Fig. 4.3. This characteristic prevents the formation of extensive graphitic planes and of a liquid mesophase.^[2]

Graphitization of Aliphatics. Chars are produced by the carbonization of aliphatic hydrocarbons (compounds with an open-ended chain) and of most polymers. They do not graphitize readily. Their turbostratic structure and the random arrangement of their crystallites (shown in Fig. 3.4 of Ch. 3) remain essentially unchanged, regardless of the temperature and duration of the heat-treatment. However, in some cases the graphitization of chars can be enhanced by a radiation treatment or by the presence of a metallic or mineral catalyst. [18] The catalytic process involves the dissolution of carbon particles at the catalyst sites and the precipitation of graphite.

Graphitization of Polymers. As mentioned above, most polymers, such as those listed in Table 4.1, are char-formers and do not graphitize to any extent (with the notable exception of polyvinyl chloride), although some reduction in the interlayer spacing (d) is usually observed. This d-spacing, however, does not shrink below 0.344 nm for most polymers. This is shown in Fig. 4.8, where the d-spacing of carbonized polyacrylonitrile (PAN) is plotted as a function of graphitization temperature. The crystallite size (L_c) remains small, going from ~ 1.5 to ~ 2.8 nm.^[19] Pitch-based fiber, on the other hand, are cokes and graphitize more readily (see Ch. 8).

During carbonization of PAN, an extensive-random network of graphitic ribbons is formed which has a stable configuration. In addition, it is speculated that some tetrahedral (sp³) (diamond) bonds are formed (which would account for the hardness of these materials).^[2] The presence of diamond structure in a similar material, diamond-like carbon, is well established (see Ch. 14). The diamond structure is reviewed in Ch. 2, Sec. 3.0. These two factors, ribbon network and tetrahedral bonds, would prevent further ordering of the structure, regardless of the graphitization temperature.

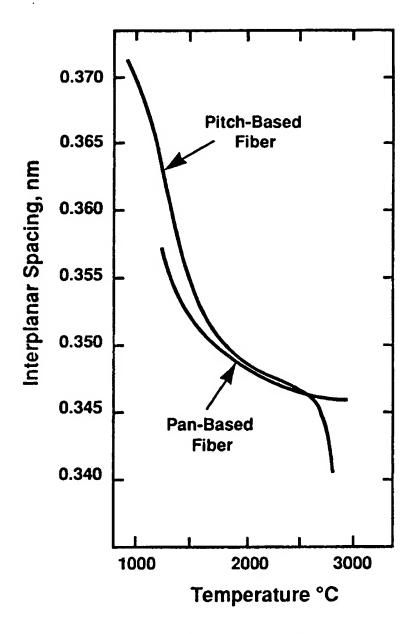


Figure 4.8. Basal plane spacing of PAN-based and pitch-based fibers as a function of graphitization temperature. [8]

Some polymeric films such as polyimide (Kapton), polyacrylonitrile (PAN) and polyfurfural alcohol, when carbonized between sheets of the mineral montmorillonite, form a two-dimensional graphitic structure with highly oriented layer planes which graphitizes readily.^{[20][21]}

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Pyrolytic Graphite

1.0 GENERAL CONSIDERATIONS

The production of molded graphite and vitreous carbon, described in the previous two chapters, relies on the carbonization (pyrolysis) of a solid, inorganic substance such as coal-tar pitch, petroleum fractions or polymers. This chapter is a review of another type of carbon material, produced by a fundamentally different process that is based on a gaseous precursor instead of a solid or liquid. The process is known as chemical vapor deposition (CVD) and the product as pyrolytic carbon or graphite, sometimes referred to as pyrocarbon or pyrographite. To simplify, in this chapter the material will be referred to as pyrolytic graphite, regardless of the degree of graphitization.

Pyrolytic graphite is different from another standpoint: although produced in bulk form, its main use is in the form of coatings, deposited on substrates such as molded graphite, carbon fibers, or porous carbon-carbon structures. As such, it is part of a composite structure and is not as readily identifiable as other forms of carbon. It is similar in this respect to CVD diamond and diamond-like carbon (DLC) described in Chs. 13 and 14.

Pyrolytic graphite is the only graphitic material that can be produced effectively as a coating. The coating can be made sufficiently thick that, after removing the substrate, a free-standing object remains.

Pyrolytic graphite is a key element in the technology of carbon and is used extensively in the coating of specialty molded graphites and in the processing of carbon-carbon components.

1.1 Historical Perspective

The CVD of carbon materials is not new. As mentioned in the pioneer work of Powell, Oxley, and Blocher, [1] its first practical use was developed in the 1880's in the production of incandescent lamps to improve the strength of filaments by carbon deposition and a patent was issued over a hundred years ago, covering the basis of the CVD of carbon. [2]

The CVD process developed slowly in the next fifty years, and was limited mostly to pyro and extraction metallurgy, and little work was done on graphite deposition.

It is only since the end of World War II that the CVD of graphite began to expand rapidly as researchers realized the potential of this technique for the formation of coatings and free-standing shapes. The importance and impact of pyrolytic graphite have been growing ever since.

1.2 The Chemical Vapor Deposition Process

CVD is now a well-established process that has reached major production status in areas such as semiconductors and cutting tools. It is a vapor-phase process which relies on the chemical reaction of a vapor near or on a heated surface to form a solid deposit and gaseous by-products. The process is very suitable to the deposition of carbon, as reviewed below.^[3]

1.3 Pyrolytic Graphite as a Coating

Although, as mentioned above, pyrolytic graphite is used by itself as free-standing structures such as crucibles or rocket nozzles (see Sec. 4.0), its major use is in the form of coatings on substrates such as molded graphite, carbon foam, carbon fibers, metals, and ceramics.

Composite Nature of Coatings. The surfaces of many materials exposed to the environment are prone to the effects of abrasion, corrosion, radiation, electrical or magnetic fields, and other conditions. These surfaces must have the ability to withstand these environmental conditions and/or provide certain desirable properties such as reflectivity, semi-conductivity, high thermal conductivity, or erosion resistance.

To obtain these desirable surface properties, a coating is deposited on the bulk material to form a composite in which bulk and surface properties may be very different.^[4]

Table 7.1 summarizes the surface properties that may be obtained or modified by the use of pyrolytic graphite coatings.

Table 7.1. Material Properties Affected by Pyrolytic Graphite Coatings

Electrical	Resistivity
Optical	Reflectivity
Mechanical	Wear Friction Hardness Adhesion Toughness
Porosity	Surface area Pore size Pore volume
Chemical	Diffusion Corrosion Oxidation

2.0 THE CVD OF PYROLYTIC GRAPHITE

The CVD of pyrolytic graphite is theoretically simple and is based on the thermal decomposition (pyrolysis) of a hydrocarbon gas. The actual mechanism of decomposition however is complex and not completely understood. This may be due in part to the fact that most of the studies on the subject of hydrocarbon decomposition are focused on the improvement of fuel efficiency and the prevention of carbon formation (e.g., soot), rather than the deposition of a coating.

Although many studies of the CVD of graphite have been carried out, a better understanding of the pyrolysis reactions, a more accurate prediction of the results, and more complete experimental, thermodynamic, and kinetic investigations are still needed.

2.1 Thermodynamics and Kinetics Analyses

The CVD of pyrolytic graphite can be optimized by experimentation. The carbon source (hydrocarbon gas), the method of activating the decomposition reaction (thermal, plasma, laser, etc.), and the deposition variables (temperature, pressure, gas flow, etc.) can be changed until a satisfactory deposit is achieved. However, this empirical approach may be too cumbersome and, for more accurate results, it should be combined with a theoretical analysis.

Such an analysis is a valuable step which, if properly carried out, predicts what will happen to the reaction, what the resulting composition of the deposit will be (i.e., stoichiometry), what type of carbon structure to expect, and what the reaction mechanism (i.e., the path of the reaction as it forms the deposit) is likely to be. The analysis generally includes two steps:

- 1. The calculation of the change in the free energy of formation for a given temperature range; this is a preliminary, relatively simple step which provides information on the feasibility of the reaction.
- 2. The minimization of the free energy of formation which is a more complete analysis carried out with a computer program.

2.2 AG Calculations and Reaction Feasibility

Thermodynamics of CVD Carbon. The CVD of carbon (as all CVD reactions) is governed by two factors: (a) thermodynamics, that is the driving force which indicates the direction the reaction is going to proceed (if at all), and (b) kinetics, which defines the transport process and determines the rate-control mechanism, i.e., how fast it is going.

Chemical thermodynamics is concerned with the interrelation of various forms of energy and the transfer of energy from one chemical system to another in accordance with the first and second laws of thermodynamics. In the case of CVD, this transfer occurs when the gaseous compounds, introduced in the deposition chamber, react to form the carbon deposit (and by-products gases).

 ΔG Calculation: The first step is to ensure that the desired CVD reaction will take place in a given temperature range. This will happen if the thermodynamics is favorable, that is, if the transfer of energy (i.e., the free-energy change of the reaction, known as ΔG_r) is negative. To calculate ΔG_r , it is necessary to know the thermodynamic properties of each component, specifically their free-energy of formation (also known as Gibbs free energy), ΔG_f . The values of ΔG_r of the reactants and products for each temperature can be obtained from thermodynamic-data tables such as the JANAF Thermochemical Tables and others. $^{[6][7]}$

It should be noted that the negative free-energy change is a valid criterion for the feasibility of a reaction only if the reaction as written contains the major species that exist at equilibrium.

2.3 Minimization of Gibbs Free Energy

Experimentation shows that the best, fully dense, and homogeneous carbon deposits are produced at an optimum negative value of ΔG . For smaller negative values, the reaction rate is very low and, for higher negative values, vapor-phase precipitation and the formation of soot can occur. Such factors are not revealed in the simple free-energy change calculation. A more complete analysis is often necessary.

A method of analysis is the minimization of the Gibbs free energy, a calculation based on the rule of thermodynamics which states that a system will be in equilibrium when the Gibbs free energy is at a minimum. The objective then is the minimization of the total free energy of the system and the calculation of equilibria at constant temperature and volume or constant pressure. It is a complicated and lengthy operation but, fortunately, computer programs are now available that simplify the task considerably.^{[8][9]}

These programs provide the following information:

- The composition and amount of deposited material that is theoretically possible at a given temperature, pressure, and concentration of input gases
- The existence of gaseous species and their equilibrium partial pressures
- The possibility of multiple reactions with the inclusion of the substrate as a possible reactant

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All of this is valuable information which can be of great help. Yet, it must be treated with caution since, in spite of all the progress in thermodynamic analysis, the complexity of many reactions in the CVD of carbon, and the fact that these calculations are based on chemical equilibrium which is rarely attained in CVD reactions, make predictions relying on thermodynamic calculations alone still questionable.

It follows that, in order to provide a reliable and balanced investigation, it is preferable to combine the theoretical calculations with an experimental program. Fortunately, carbon deposition experiments are relatively easy to design and carry out without the need for expensive equipment, and results can usually be obtained quickly and reliably.

2.4 CVD Reactions for the Deposition of Pyrolytic Graphite

The CVD reactions to deposit pyrolytic graphite are based on the thermal decomposition (pyrolysis) of hydrocarbons. The most common precursor is methane (CH₄), which is generally pyrolyzed at 1100°C or above, over a wide range of pressure from about 100 Pa (0.001 atm) to 10⁵ Pa (1 atm). The reaction in a simplified form is as follows:^{[1][10][11]}

Eq. (1)
$$CH_4 \rightarrow C + 2H_2$$

Other common precursors are ethylene (C_2H_6) and acetylene (C_2H_2).^{[1][12]} Acetylene can also be decomposed at lower temperature (300 - 750°C) and at pressures up to 1 atm, in the presence of a nickel catalyst.^[12] Another common precursor is propylene (C_3H_6) which decomposes in the 1000 - 1400°C temperature range at low pressure (~ 1.3 x 10⁴ Pa or 100 Torr).^[13]

The activation energies for the decomposition of these precursor gases still are not accurately known and show a considerable scatter. The reported values are as follows:

Methane 78 - 106 kcal/g·mole

Ethane 60 - 86 kcal/g·mole

Acetylene 30 - 50 kcal/g·mole

Deposition Mechanism: The pyrolysis of a hydrocarbon, such as shown in reaction equation (1), is actually a series of more complex reactions involving molecules of gradually increasing size. A possible mechanism of deposition of pyrolytic graphite is deduced from a series of experiments carried out in the apparatus shown in Fig. 7.1.^[5]

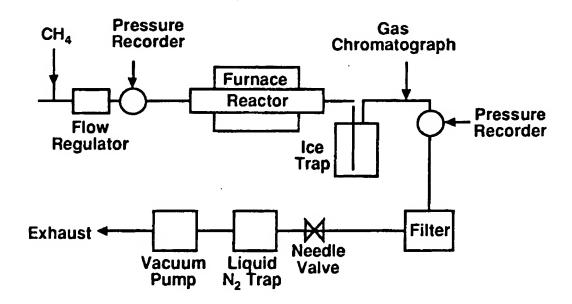


Figure 7.1. Schematic of experimental apparatus for the production of pyrolytic graphite. [5]

In this study, a spectrographic analysis of the by-products of the decomposition of methane revealed the presence of large amounts of acetylene, ethylene, and benzene, plus a variety of compounds consisting mostly of the polyaromatic hydrocarbons (PAH) such as naphthalene, anthracene, phenantrene, acenaphthylene, pyrene, and fluoranthene, in addition to the deposited pyrolytic graphite. Some of these compounds form the soot and tar-like deposits which are often observed on the wall of CVD reactors during carbon deposition.

It is generally agreed that the following simplified deposition sequence is taking place: [5][14]

Methane → Benzene → Polyaromatic hydrocarbons → Carbon

2.5 Deposition Systems and Apparatus

A common CVD apparatus for the deposition of pyrolytic graphite is the so-called cold-wall reactor. This reactor does not require a furnace since the substrate to be coated is heated directly, usually by induction heating.

The decomposition reactions for the deposition of pyrolytic graphite are endothermic, i.e., they absorb heat. As a result, deposition takes place preferentially on the surfaces where the temperature is the highest, in this case the substrate, while the cooler walls of the reactor remain essentially uncoated.

A simple laboratory type reactor for pyrolytic-graphite deposition is shown in Fig. 7.2.^[3] The substrate is a molded-graphite disk which is rotated to improve deposition uniformity. It is heated by a high-frequency (450 kHz) induction coil and deposition occurs at low pressure (500 Pa). Temperature is monitored and controlled by a sheathed thermocouple and corroborated by an optical pyrometer.

Production systems of a similar basic design now reach considerable size, with CVD furnaces 1.2 m in diameter and over 2 m high commercially available.

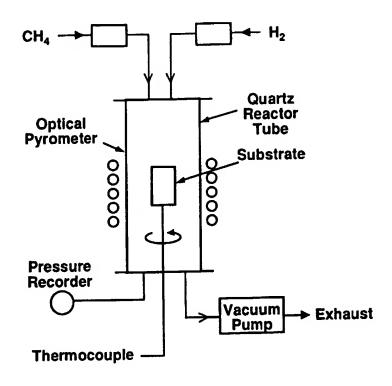


Figure 7.2. Schematic of a cold-wall reactor for the production of pyrolytic graphite. [3]

2.6 Chemical Vapor Infiltration (CVI)

Chemical vapor infiltration (CVI) is a special CVD process in which the gaseous reactant infiltrates a porous material such as an inorganic open foam or a fibrous mat or weave. The deposition occurs on the fiber (or the foam), and the structure is gradually densified to form a composite.^[15]

CVI has the same chemistry and thermodynamics as conventional CVD, but the kinetics is different since the reactants have to diffuse inward through the porous structure and the by-products of the reaction have to diffuse out.^[16] The process is used extensively in the production of carbon-carbon materials, reviewed in Ch. 9.^[17]

2.7 Fluidized-Bed CVD

Fluidized-bed CVD is a special technique which is used primarily in coating particles such as nuclear fuel. A flowing gas imparts quasi-fluid properties to the particles. Fig. 7.3 shows a typical fluidized-bed CVD reactor.^[3]

The fluidizing gas is usually methane, helium, or another non-reactive gas. Factors to consider to obtain proper fluidization are the density and size of the particles to be coated, and the velocity, density, and viscosity of the gases. [18] If the velocity is too low, the particles will fall into the gas inlet; if it is too high, they will be blown out of the bed. Heavy or large objects may require suspension in the bed.

The gas velocity, $V_{\rm m}$, is given by the following relationship:

$$V_m = d^2 (\rho_p - \rho_g) G / 1650 \mu$$
 [for $dV_o \rho_g / \mu < 20$]

where:

d = particle diameter

 ρ_p = particle density

 ρ_g = gas density

G = acceleration of gravity

V_o = superficial gas velocity

 μ = gas viscosity

The major applications of pyrolytic carbon deposited by fluidized bed are found in the production of biomedical components such as heart valves and in the coating of uranium carbide and thorium carbide nuclear-fuel

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particles for high temperature gas-cooled reactors, for the purpose of containing the products of nuclear fission. The carbon is obtained from the decomposition of propane (C_3H_8) or propylene (C_3H_6) at 1350°C, or of methane (CH_4) at 1800°C.^[1] Its structure is usually isotropic (see Sec. 3.5).

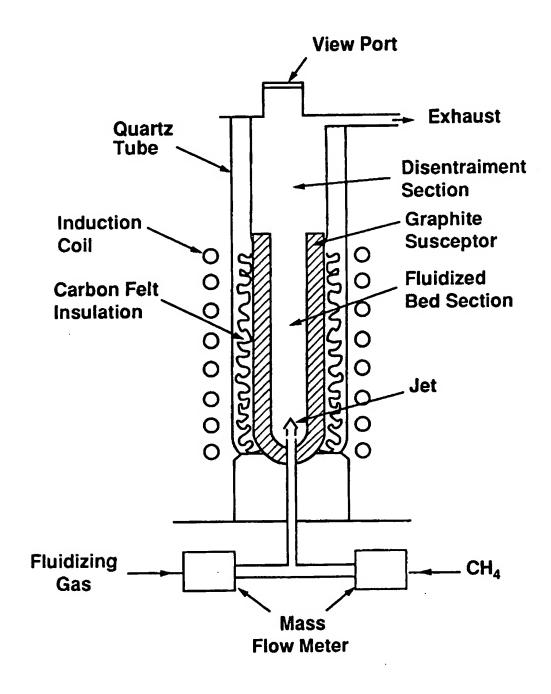


Figure 7.3. Schematic of a fluidized-bed CVD reactor for the deposition of pyrolytic graphite.^[3]

2.8 Plasma CVD

7

The deposition of graphite can also be obtained by plasma CVD, with the following characteristics:^[19]

Gases: propylene-argon or methane-argon

Plasma: radio frequency (RF) at 0.5 MHz

• Pressure: <1300 Pa

■ Temperature: 300 - 500°C

In a plasma-activated reaction, the substrate temperature can be considerably lower than in thermal CVD. This allows the coating of thermally sensitive materials. The characteristics, and properties of the coating are similar to those of coatings deposited at higher temperatures (>1000°C).

Plasma activation is also used extensively in the deposition of polycrystalline diamond and diamond-like carbon (DLC). It is reviewed in more detail in Chs. 13 and 14.

3.0 STRUCTURE OF PYROLYTIC GRAPHITE

3.1 The Various Structures of Pyrolytic Graphite

Pyrolytic graphite is an aggregate of graphite crystallites which have dimensions (L_c) that may reach several hundred nm (see Ch. 3, Sec. 2). It has a turbostratic structure, usually with many warped basal planes, lattice defects, and crystallite imperfections.

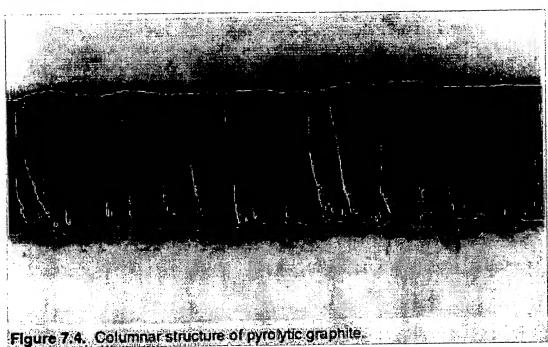
Within the aggregate, the crystallites have various degrees of orientation. When they are essentially parallel to each other, the nature and the properties of the deposit closely match that of the ideal graphite crystal.

The structure of a pyrolytic graphite deposit can be either columnar, laminar, or isotropic, depending on the deposition conditions such as temperature, pressure, and composition of the input gases. [1][10][14][20] It is possible to obtain the desired structure by the proper control of these deposition parameters.

3.2 Columnar and Laminar Structures

Columnar Structure. The columnar structure of pyrolytic graphite is shown in Fig. 7.4. The crystallites are deposited with the basal planes (ab

directions) essentially parallel to the deposition surface. Their structure tends to be columnar (cone-like) as a result of uninterrupted grain growth toward the reactant source.



Effect of Substrate Geometry. The smoothness of the substrate is a very critical factor. Fig. 7.5 shows schematically the growth of the graphite deposit above a convex surface defect of the substrate such as a surface asperity or a dust particle. The deposit tends to magnify any such surface imperfection and, to obtain a uniform pyrolytic graphite growth, a perfectly smooth and clean surface is necessary.[11]

Continuous Nucleation. The structure is also often dependent on the thickness of the deposit. For instance, the grain size increases as the thickness increases and the columnar-grain structure becomes more pronounced as the film becomes thicker. Such large columnar structures are usually undesirable as the deleterious effects of grain growth and columnar formation can be considerable, causing structural failure and the rapid diffusion of impurities along grain boundaries.

Large grain size can be avoided by continuously adding growth sites, where new columnar growth can be generated. This effect is shown schematically in Fig. 7.6. These new growth sites originate from soot particles, which are formed in the gas-phase when the pressure and supersaturation are above a certain level.[11][14]

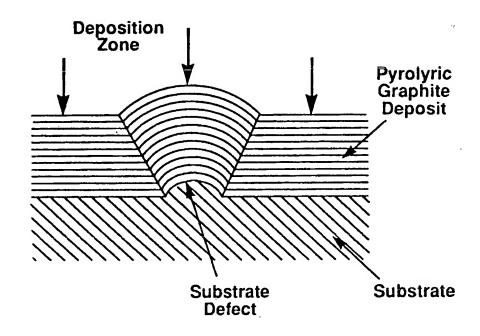


Figure 7.5. Effect of substrate defect on deposited structure of pyrolytic graphite. [11]

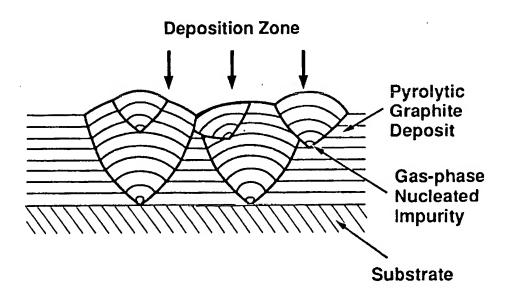


Figure 7.6. Effect of gas-phase nucleated impurities on deposited structure of pyrolytic graphite.[11]

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Laminar Structure. The laminar structure of pyrolytic graphite consists of essentially parallel layers (or concentric shells if deposited on a particle or fiber). It is shown in Fig. 7.7.

Both columnar and laminar structures are optically active to polarized light and usually have similar physical properties.^{[10][14]}

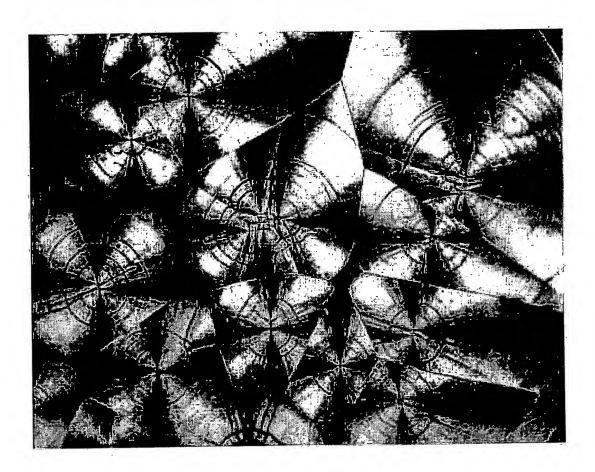


Figure 7.7. Laminar structure of pyrolytic graphite, deposited on carbon filament (Photograph courtesy of Jack Chin, La Costa, CA.)

3.3 Isotropic Structure

The other type of pyrolytic structure, isotropic carbon, has little graphitic characteristic and essentially no optical activity. It is composed of very fine grains without observable orientation and for this reason, it is known as isotropic carbon rather than isotropic graphite. It is often obtained in fluidized-bed deposition, possibly due to continuous surface regeneration by the mechanical rubbing action of the bed. An isotropic structure, observed by transmission electron microscopy, is shown in Fig. 7.8.^[21]



Figure 7.8. High-density (~ 2.0 g/cm³) isotropic structure of pyrolytic carbon, observed by transmission electron microscopy. Viewing plane is parallel to deposition plane (x=23,600). (Photograph courtesy of J. L. Kaae, General Atomics, San Diego, CA.)

3.4 Effect of Deposition Parameters

Effect of Pressure. Pyrolytic-graphite coatings with more uniformity, better coverage, and improved quality are generally obtained at low deposition pressure. Pressure controls the thickness of the surface boundary layer and consequently the degree of diffusion. By operating at low pressure, the diffusion process can be minimized and surface kinetics becomes rate-controlling. [3] Low-pressure deposition tends to be isotropic.

At higher pressure (i.e., atmospheric), the reactant gas must be diluted with an non-reactive gas such as hydrogen or argon to prevent uncontrolled vapor-phase precipitation, while generally no dilution is necessary at low pressure. However, atmospheric pressure reactors are simpler and cheaper, and, with proper control of the deposition parameters, satisfactory deposits can be obtained.

7

Effect of C/H Ratio. The C/H ratio of the gas mixture (CH₄, and H₂) entering the reaction chamber is an important factor in the control of the nature of the deposition. Higher C/H ratios (1/4) favor laminar deposition and lower ratios (1/14) favor isotropic deposition. [10]

Effect of Temperature. Generally, isotropic deposits are obtained at higher temperatures (>1400°C) and laminar and columnar deposits at lower temperatures.

In summary, isotropic deposits are obtained at high temperature, low pressures, and low carbon-to-hydrogen (C/H) ratio. The opposite conditions favor the deposition of laminar and columnar deposits.

3.5 Heat-Treatment and Graphitization

The mechanism of graphitization of pyrolytic graphite is essentially the same as that of pitch coke, described in Ch. 4, Sec. 3.3.^[22]

Graphitization of Columnar and Laminar Deposits. The columnar and laminar deposits described above have generally a turbostratic structure in the as-deposited condition, with a large interlayer spacing (~ 0.344 nm) as revealed by x-ray diffraction. The material graphitizes readily when heat-treated at 2500°C for 90 minutes.

The 2500°C heat-treatment causes the reordering of the structure. The basal planes coalesce and become more parallel and closer together. The various crystallite imperfections such as vacancies, stacking faults, dislocations, and rotational disorders, tend to heal and disappear; the crystallite size (L_c) increases; the 002 line narrows considerably and becomes close to the position of the ideal graphite line as the interlayer spacing (d) decreases to approach that of the ideal graphite crystal (0.3354 nm). This observed reduction of the interlayer spacing is attributed in part to the removal of interstitial elements, mostly carbon.^[22]

When columnar or laminar pyrolytic graphites are annealed above 2700° C, usually under a pressure of several atmospheres, further ordering and stress relieving of the structure occur within each plane and between planes. The material is known as "highly oriented pyrolytic graphite (HOPG)". It is soft and structurally close to the ideal graphite crystal with an angular spread of the c axes of crystallites of less than one degree. [23]

Graphitization of Isotropic Deposits. Unlike columnar and laminar pyrolytic deposits, isotropic carbon does not graphitize readily and is, in this respect, similar to vitreous carbon. Some reduction in the interlayer spacing

(d) is usually observed, but rarely does it decreases below 0.344 nm. The crystallite size (L_c) remains small.

4.0 PROPERTIES OF PYROLYTIC GRAPHITE

7

4.1 Properties of Columnar and Laminar Pyrolytic Graphites

The structure of both columnar and laminar pyrolytic graphites is close to that of the ideal graphite crystal (reviewed in Ch. 3, Secs. 3 and 4). These graphites have a high degree of preferred crystallite alignment particularly after heat-treatment, and their properties tend to be anisotropic. Melting point, sublimation point, heat of vaporization, entropy, enthalpy, specific heat, and chemical properties are similar to that of the single-crystal graphite but other properties may vary significantly (Ch. 3, Sec. 7).

The properties of pyrolytic graphite are summarized in Table 7.2. The values listed were collected from the manufacturer's data sheets. [24]-[27] The spread in value may represent slightly different materials and differences in the degree of graphitization. It may also reflect variations in the test methods; for instance, the measurement of mechanical properties may vary widely depending on the sample geometry and the test method (see Ch. 5, Sec. 2.1).

Table 7.2. Properties of Oriented Pyrolytic Graphite at 25°C

7.2. Properties of Offerted 1 yrolyto diaprile at 25 5				
Density, g/cm ³	2.10 - 2.24			
Flexural strength tested in the c direction (across grain), MPa	80 - 170			
Tensile strength tested in the ab directions (with grain), MPa	110			
Young's modulus of elasticity, GPa	28 - 31			
Thermal conductivity, W/m·K c direction ab directions	1 - 3 190 - 390			
Thermal expansion 0 - 100°C, x10 ⁻⁶ /r c direction ab directions	n·K 15 - 25 -1 to 1			
Electrical resistivity, $\mu\Omega$ ·m c direction ab directions	1000 - 3000 4 - 5			

7

Mechanical Properties. The mechanical properties of pyrolytic graphite are like those of the ideal graphite crystal in the sense that they show a marked increase with increasing temperature as shown in Fig. 7.9.^{[11][26]} Above 2600°C, the strength drops sharply.

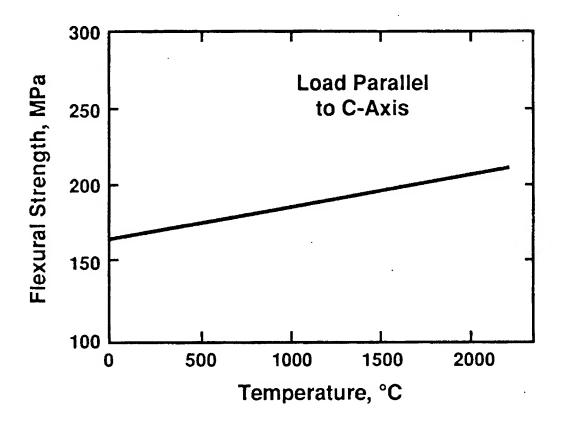


Figure 7.9. Flexural strength of pyrolytic graphite as a function of temperature.[11]

Thermal Conductivity. As noted in Ch. 3, Sec. 4.3, the thermal conductivity of the ideal graphite crystal in the *ab* directions is high. It is far lower for the average pyrolytic graphite (up to 390 W/m·K at 25°C) but still high enough for the material to be considered a good thermal conductor, similar to copper (385 W/m·K at 25°C) (see Ch. 3, Table 3.6).

The thermal conductivity in the *c* direction is approximately 2.0 W/m·K at 25°C and, in this direction, graphite is a good thermal insulator, comparable to most plastics. The anisotropy ratio is approximately 200.

The thermal conductivity in both the aband c directions decreases with temperature as shown in Fig. 3.12 of Ch. 3.

Thermal Expansion. The thermal expansion of pyrolytic graphite, like that of the ideal graphite crystal, has a marked anisotropy. It is low in the *ab* directions (lower than most materials) but an order of magnitude higher in the *c* direction. The effect of temperature is shown in Fig. 7.10. Such a large anisotropy may lead to structural problems such as delamination between planes, especially in thick sections or when the material is deposited around a sharp bend.

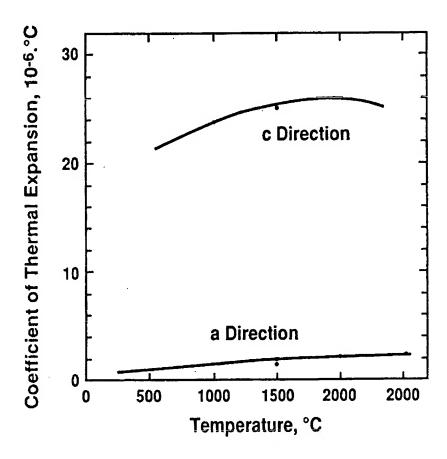


Figure 7.10. Coefficient of thermal expansion (CTE) of pyrolytic graphite as a function of temperature. [24]

Electrical Properties. The electrical properties of pyrolytic graphite also reflect the anisotropy of the material and there is a considerable difference between the resistivity in the *ab* and the *c* directions. Pyrolytic graphite is considered to be a good electrical conductor in the *ab* directions, and an insulator in the *c* direction. Its electrical resistivity varies with temperature as shown in Fig. 7.11.

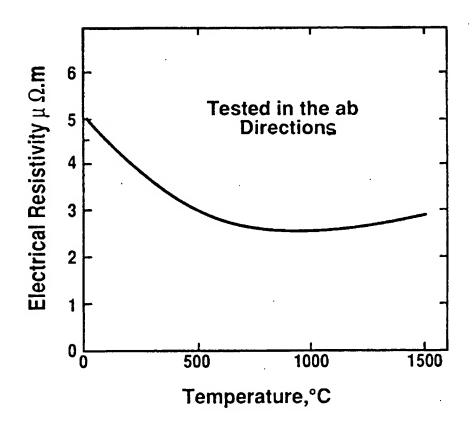


Figure 7.11. Electrical resistivity of pyrolytic graphite as a function of temperature. [26]

4.2 Properties of Isotropic Pyrolytic Carbon

As mentioned above, the structure of pyrolytic carbon is essentially isotropic and so are its properties. These are summarized in Table 7.3.

Hardness. Being composed of minute crystallites with essentially random orientation, isotropic pyrolytic carbon lacks the easy interlayer slippage which is characteristic of the well-oriented laminar or columnar structures of pyrolytic graphite. As a result, it is considerably harder. This makes it easy to polish and the material can be given a high gloss. The wear resistance is usually superior to that of the columnar and laminar deposits of vitreous carbon.^[25]

Mechanical Properties. Isotropic pyrolytic carbon is stronger than the oriented pyrolytic graphites and vitreous carbon and can be considered as a reasonable structural material, comparing favorably with some of the more brittle ceramic materials.

Table 7.3. Properties of Isotropic Pyrolytic Carbon at 25°C (as deposited)

Density, g/cm ³	2.1		
Vickers DPH* hardness, kg/mm ²	240 - 370		
Flexural strength, MPa	350		
Young's modulus, GPa	28		
Strain to failure, %	1.2		
* DPH: diamond pyramid hardness			

Gas Permeability. Isotropic pyrolytic carbon provides a better barrier to gases than the more crystalline pyrolytic graphites.^[26] The permeability, K, is as follows:

Isotropic pyrolytic carbon: 10⁻⁶ to 10⁻¹⁵ cm²-s

Pyrolytic graphite: 10⁻² to about 10 cm²·s

5.0 APPLICATIONS OF PYROLYTIC GRAPHITE AND CARBON

5.1 High-temperature Containers and Other Free-Standing Products

Containers and other free-standing (monolithic) parts are produced by depositing the pyrolytic carbon or graphite onto a graphite mandrel. After the deposition is completed, the mandrel is removed, usually by machining.

It is difficult to deposit pyrolytic graphite in shapes having sharp radii without interlayer delaminations. These delaminations are caused by the stresses generated by the considerable differences in the thermal expansion in the *ab* and *c* directions which can overcome the low interlaminar strength. These delaminations do not occur with isotropic pyrolytic carbon.

Common applications of pyrolytic graphite are:

- Boats, and crucibles for liquid-phase epitaxy
- Crucibles for molecular-beam epitaxy
- Reaction vessels for the gas-phase epitaxy of III-V semiconductor materials such as gallium arsenide
- Trays for silicon-wafer handling

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Free-standing isotropic pyrolytic carbon is a material of choice for solid propellant rocket nozzles. Because of its strength, hardness, and isotropic nature, it is able to withstand the mechanical erosion which is the dominant failure mechanism above 3200°C. [27]

5.2 Resistance-Heating Elements

Because of its good electrical characteristics and refractoriness, pyrolytic graphite is used extensively for high-temperature resistance-heating elements. In combination with pyrolytic boron nitride (PBN), it provides an integrated heating system in which the graphite is the resistive element and PBN the insulating substrate. Both materials are produced by CVD. The product is used as a source heater in metal evaporation and semiconductor epitaxy, as a substrate heater in thin-film deposition, as a melt heater for crystal growth, and in other applications.^[28]

5.3 Nuclear Applications

Isotropic pyrolytic carbon exhibits excellent stability under neutron irradiation. This, coupled with its high strength, dense isotropic structure, and impermeability to gases, makes it the material of choice for the coating of nuclear fission particles to contain the fission products.^{[1][24]} The coating is produced in a fluidized bed (see Sec. 2.7 above).

5.4 Biomedical Applications

Biomedical applications require a material with good strength, fatigue-resistance, high erosion resistance, chemical inertness, and compatibility with blood and tissues. Isotropic pyrolytic carbon meets these criteria and is used extensively in biomedical devices such as heart valves and dental implants where its performance is superior to other forms of carbon such as pyrolytic graphite or vitreous carbon.^[25]

5.5 Coatings for Molded Graphites

A pyrolytic graphite coating, applied to a molded graphite substrate, provides a smooth, essentially pore-free surface that can enhance the chemical resistance. Such coated parts are found in applications requiring

chemical inertness at high temperature (in a non-oxidizing atmosphere) such as the following:

- Wafer trays for plasma-CVD equipment
- Boats for liquid-phase epitaxy
- Boats, and other parts for vapor deposition of III-V semiconductor compounds such as gallium arsenide
- Hardware for metal processing

5.6 Coatings for Fibers

(n 4)

Inorganic fibers, such as silicon carbide or alumina, provide the reinforcement for metal or ceramic matrices to form refractory composites. These fibers often react with the matrix material during processing into composites or during operation at high temperature. This interaction produces intermetallics or other compounds which may considerably degrade the properties of the composite. A pyrolytic graphite coating applied on the fiber acts as a diffusion barrier, and prevents these diffusional reactions (see Ch. 9, Secs. 5.0 and 6.0).^{[3][29]}

Another fiber coating application is found in fiber optics. An isotropic pyrolytic-carbon coating is applied on optical fibers to improve the abrasion and fatigue resistance, and bending performance.^[30]

5.7 Carbon-Carbon Infiltration

Pyrolytic carbon or graphite is used to densify carbon-carbon structures by infiltration as described in Sec. 2.6 above. Applications include reentry heat shields, rocket nozzles, aircraft disk brakes, and other aerospace components.^[17] This topic is reviewed in more detail in Ch. 9.

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- Low density (2.1 2.3 g/cm³, depending on the type)
- Optically opaque even in extremely thin sections
- Chemically stable at ordinary temperature
- Unaffected by weathering (as evidenced by bright flakes found in disintegrated graphite-bearing rocks)
- High thermal and electrical conductivity
- Low coefficient of thermal expansion
- Low coefficient of friction
- Greasy feel

1.2 Types of Natural Graphite

Natural graphite is classified into three general types: flake (also known as *plumbago*), crystalline (vein), and amorphous, varying in physical properties, appearance, chemical composition, and impurities. These differences stem from the type of precursor material (oil, coal, or other carbonaceous deposits) and the natural process by which graphite was formed. Table 10.2 summarizes the characteristics of these three types.^{[2][3]}

Table 10.1. Characteristics and Properties of the Three Types of Natural Graphite

	Туре		
Property	Flake	Crystalline	Amorphous
Composition			
Carbon, %	90	96	81
Sulfur, %	0.10	0.70	0.10
Density, g/cm ³	2.29	2.26	2.31
Degree of			
graphitization, %	99.9	100	28
d-spacing (002), nm	0.3355	0.3354	0.3361
Resistivity, Ω·cm	0.031	0.029	0.091
Morphology	Plate	Plate Needle	Granular